

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM

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PROCEEDINGS OF THE  
SECTION OF SCIENCES

VOLUME XXVIII

PUBLISHED BY  
KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN, AMSTERDAM  
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Natuurkunde, Vols. XXXIII and XXXIV).

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM

PROCEEDINGS

VOLUME XXVIII

Nº. 1

President: Prof. F. A. F. C. WENT

Secretary: Prof. L. BOLK

(Translated from: "Verslag van de gewone vergaderingen der Afdeeling  
Natuurkunde", Vol.s XXXIII and XXXIV)

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**Chemistry.** — *"The Metastability of the Elements and Chemical Compounds in consequence of Enantiotropy or Monotropy, VIII.*  
By Prof. ERNST COHEN and Dr. W. D. HELDERMAN.

(Communicated at the meeting of June 28, 1924.)

1. In our fourth paper on the subject under the above title<sup>1)</sup> it was shown, that BRIDGMAN's determination of the change of volume which takes place when ammonium nitrate passes from IV into III (at 32°.3 C.) has an error of about 9<sup>0</sup>/<sub>0</sub>, and this in consequence of the persistent retardations which can occur during this transformation. This was quantitatively another proof that the physical constants of solid substances which we know up to the present moment generally relate to metastable mixtures of unknown composition of the modifications of those substances. At the same time it was again insisted upon that no confidence can be put in those constants, unless they are determined for the pure modifications.

It stands to reason (in the paper above mentioned it was indeed pointed out) that values, calculated with those constants that have been thus erroneously determined, are also wrong, unless accidental compensation of experimental errors should have played a part in the calculation.

Now BRIDGMAN<sup>2)</sup> in his investigation mentioned above has found: 4.66  $\frac{\text{gr. calories}}{\text{gm.}}$  for the transition heat III  $\rightarrow$  IV at the transition point, by means of data he experimentally determined:

$$\left( \frac{dT}{dp} = 0.0311 \frac{\text{degree}}{\text{kg.cm.}}; (v_{III} - v_{IV}) = 0.02026 \frac{\text{ccm.}}{\text{gr.}} \right)$$

according to the equation of CLAPEYRON—CLAUSIUS:

$$\frac{dT}{dp} = \frac{T(v_{III} - v_{IV})}{W}$$

The question now arises: is this figure correct, or has it, just like the value  $(v_{III} - v_{IV})$  determined by BRIDGMAN, as great an error (about 9<sup>0</sup>/<sub>0</sub>)? From the way he made his  $\frac{dT}{dp}$  determinations<sup>3)</sup> it is obvious that they

<sup>1)</sup> These Proceedings, 27, 65 (1924); Zeitschr. f. physik. Chemie 109, 81 (1924).

<sup>2)</sup> Proc. Americ. Acad. of Arts and Sciences 51, 581 (1916).

<sup>3)</sup> Proc. Americ. Acad. of Arts and Sciences 51, 55 (1915); Phys. Rev. 3, 126 (1914); 6, 1 (1915).

were fixed with sufficient accuracy. Consequently it was necessary that the transition heat at the transition temperature should be most accurately determined.

2. It is true, that BELLATI and ROMANESE <sup>1)</sup> have found for it the value of  $5.02 \frac{\text{gm. cal.}}{\text{gm.}}$ , but it is not sufficiently certain that they made their investigations with the pure modification III and IV, while moreover many objections may be raised against the method they followed. Their manner of procedure was as follows:

First of all they determined the transition point by the thermometrical method. By heating this was found to be  $35^\circ$ , by cooling  $31^\circ$ . Quite arbitrarily they fixed the transition temperature at  $31^\circ$ . Then the mean specific heat of modification IV between 0 and  $26^\circ$  was determined by putting weighed quantities of it in a calorimeter, filled with turpentine, and determining the consequent accompanying heat effect. The same procedure was then carried out with modification III in a temperature interval from  $82-31^\circ$ , cooling it from a higher temperature than the transition point to one below this temperature. The results thus obtained are found in table I.

TABLE I.

Nº.	$T$	$t$	$Q$
1	$0^\circ,05$	$24^\circ,79$	10.00
2	0.17	25.79	10.28
3	0.18	26.13	10.76
4	39.99	27.10	9.95
5	39.84	25.74	10.13
6	78.3	27.55	23.04
7	80.9	27.00	24.58

Here  $T$  and  $t$  represent the initial, respectively the final temperature of the salt, and  $Q$  the amount of heat given off, when one gram of the salt was cooled from the higher temperature down to the lower.

3. *Diagrammatically* BELLATI and ROMANESE have found from these data:

mean specific heat between 0 and  $31^\circ$  of modification IV : 0.407

“ “ “ “ “ 31 “  $82^\circ,5$  “ “ “ II : 0.355

Heat of transition III  $\rightarrow$  IV at  $31^\circ$  : 5.02 gm. cal. per gram  $\text{NH}_4\text{NO}_3$ .

<sup>1)</sup> Atti del R. Istituto Veneto (6) 4, 1395 (1886); also Il nuovo Cimento (3) 21, 1 (1887).

By *computation* we find from the above table:

From experiment 1 : mean specific heat IV : 0.404	} mean 0.407
"      "      2 : "      "      "      IV : 0.401	
"      "      3 : "      "      "      IV : 0.415	

The divergencies between the different experiments therefore are not inconsiderable.

Further the computation gives:

Mean specific heat III : 0.356.

Heat of transition III  $\rightarrow$  IV 4.99 gram calories per gram  $\text{NH}_4\text{NO}_3$ .

The objections against calculating the heat of transition at the transition temperature by means of the mean specific heats of the two modifications, determined for great temperature intervals above and below the transition temperature instead of by means of the true spec. heat of those modifications at the temperature of transition, are obvious.

4. Some time ago, when our investigations had already begun, MONDAIN MONVAL<sup>1)</sup> gave a second, more incidental determination of the heat of transition when he calculated from his investigations this heat effect as the difference of the fictitious heats of solution of the modifications III and IV of ammonium nitrate at the transition temperature. His determinations however are such (we hope to return to this subject in another connection later on), that a priori not much value can be attached to his results.

#### *The Method employed.*

5. When, of the two pure modifications III and IV at the transition temperature (which according to our previous investigations lies at 32°.<sub>3</sub> at 1 atm. pressure), we determine the heat of solution in some medium, taking care that the final state is the same for equal quantities of the two modifications, the difference of these heats of solution gives us the desired heat of transition at the temperature of the experiment.

In connection with another investigation which will be described later on, we have experimentally fixed the curves which at the transition temperature represent the intermediate heats of solution of the modifications III and IV as function of the concentrations of aqueous solutions of ammonium nitrate. If these ordinates represent these intermediate heats of solution (per mole), the abscissae the concentrations of the solutions used, the desired heat of transition (per mole) is equal to the difference of the ordinates of any pair of points in the two curves which have the same abscissa.

<sup>1)</sup> C. R. Paris 177, 175 (1923).

*The Materials used.*

6. An already very pure commercial preparation was recrystallized a few times from distilled water. Then impurities could not be found in 10 gm<sup>1</sup>). A solution of the last crystallization, saturated at 100°, was filtered through a hot water funnel and allowed to stand. From the salt crystallized out we prepared some kilograms of each of the two pure modifications III and IV.

*a. Modification III.*

(Region of Stability 32°.3 — 84°.2 C.).

7. As will appear from what follows special precautions are absolutely necessary for the preparation of the different modifications and the control whether the pure modification, one expects to have, is present. If these precautions are not taken the investigator exposes himself to many complications during the calorimetric measurements. Modification III has been prepared in two different ways. (Preparation III A and III B.)

8. (Preparation III A). Part of the salt, mentioned in par. 6, which had crystallized from a saturated solution at 100°, between this temperature and 18°, was placed in moist condition in a drying oven, in which it was kept at 75° for two months. From time to time it was powdered very fine in a mortar in order to renew the surface and to open vacuoles which eventually might be present. Finally we transferred it to an desiccator, in which it was kept at about 40° for a few weeks over P<sub>2</sub>O<sub>5</sub>. From this stock we continually used a part for the caloric experiments.

9. In order to make sure that the salt, thus prepared, was really the pure modification III, we determined the density at 32°.3 (the transition temperature). ERNST COHEN and J. KOOY<sup>2</sup>) had found for it  $d_{40}^{32.3} = 1.654$ , whereas the density of modification IV is  $d_{40}^{32.3} = 1.716$ . We used xylene in the pycnometer as liquid which previously had been distilled in presence of P<sub>2</sub>O<sub>5</sub>.

In two independent determinations with two different pycnometers, we found for our preparation  $d_{40}^{32.3} = 1.701$  and 1.701, the next day, with a new quantity of salt 1.700. For all the determinations we used about 15 gm. of salt. When the salt of the last determination had been for 24 hours in contact with xylene in the pycnometer, we found  $d_{40}^{32.3} = 1.705$ .

10. Now it was possible that our preparation III A had originally been the pure modification III, but that during the pycnometric determination

1) E. MERCK, Prüfung chemischer Reagentien auf Reinheit, 2. Aufl. 1912, S. 73.

2) These Proceedings, 27, 65 (1924); Zeitschr. f. physik. Chemie 109, 82 (1924).

a partial transformation into IV had taken place. According to former investigations with cadmium iodide <sup>1)</sup> it did not seem probable that the dry salt in the pycnometer during weighing (at room temperature) had stabilized — partially or totally — to IV, but it was possible that III had partially been transformed into IV, after xylene at room temperature had been added in the pycnometer, and the apparatus had been heated in a thermostat to 32°.3, and had been evacuated. That this was indeed the case was proved by the experiments which we made with a new preparation of modification III (III B).

11. The preparation of III B was as follows:

A large quantity of recrystallized  $\text{NH}_4\text{NO}_3$  was totally dissolved and placed in a crystallizing dish in a drying oven which was kept at 60°. After 4 days and nights the salt was dry; it was powdered and kept over  $\text{P}_2\text{O}_5$  in a desiccator at 60°. After 4 days and nights we determined the density in the following way:

When the dry salt had been weighed in the pycnometer, we placed the latter in the thermostat at 32°.3. When the salt had assumed this temperature, we filled up the pycnometer with the xylene, mentioned above, which had previously likewise been heated to 32°.3. We found now:  $d_4^{32.3} = 1.651$  and  $1.653$ .

So the preparation was indeed the pure modification III, and is metastable at room temperature.

Our large stock of this preparation which was used later on in the caloric experiments, was always kept in a desiccator over  $\text{P}_2\text{O}_5$  at 60°.

12. In order to prove that the manipulations for the determinations of the density of III A really might have given rise to partial stabilization, the density at 32°.3 of two quantities of III B was investigated, just as had been done with III A, that is to say: after weighing the dry salt in the pycnometers at room temperature, xylene, not previously heated, was added to them. Then the pycnometers were placed in the thermostat at 32°.3. Now we found  $d_4^{32.3} = 1.693$  and  $1.698$ . Partial stabilization had indeed taken place.

#### *b. Modification IV.*

(Region of Stability — 16° up to 32°.3 C.).

13. This preparation was also obtained in two different ways (IV A and IV B), IV A in the following manner:

The moist salt, crystallized from a solution saturated at 100° between that temperature and 18° was placed under a desiccator jar by the side

<sup>1)</sup> ERNST COHEN and A. L. TH. MOESVELD, Verslag afd. Natuurkunde Kon. Akademie v. Wet. 28, 581, 602 (1920) Zeitschr. f. physik. Chemie 94, 471, 482 (1920).

of a dish filled with water. When it had remained for a month at  $18^{\circ}$ , we substituted sulphuric acid for the water, and removed the air from the jar. Every day the salt was stirred. After two weeks we replaced the sulphuric acid by  $P_2O_5$ , and then dried for six weeks more. During this period the salt was powdered in a mortar every two days. At last we determined the density at  $32^{\circ}.3$ , observing the precautions mentioned with preparation III B (par. 11).

We found:  $d_{40}^{32.3} = 1.713$  and  $1.714$ , whereas, according to the determinations of ERNST COHEN and J. KOOY<sup>1)</sup>, at that temperature the density is  $1.716$ . It may be remarked that more confidence is to be placed in the latter figure than in the one found with the pycnometer, the accuracy of which is here only about 3 units of the third decimal place.

So we infer that our preparation IV A is a pure modification IV. It was kept over  $P_2O_5$  in a desiccator at room temperature. In the caloric experiments we continually used part of it. In the last experiments (see Table II) with the solutions of 68.75 per cent we experimented with a freshly prepared preparation of IV, the density of which was  $d_{40}^{32.30} = 1.716$ .

14. During a second preparation of modification IV (preparation IVB), we had experiences which may serve as a warning. We started with a quantity of  $NH_4NO_3$  which for some time had been heated above the transition point. In order to stabilize the whole mass to IV, we moistened it with water, and let it stand at  $18^{\circ}$ . After a few days we dried the salt in vacuo over sulphuric acid, then over  $P_2O_5$ . In two independent determinations we found  $d_{40}^{32.3} = 1.647$ .

As from our investigations on cadmium iodide we knew<sup>2)</sup> that this salt easily stabilizes when it is in contact with toluene, distilled in presence of  $P_2O_5$ , we tried to accelerate the transformation of  $NH_4NO_3$  into IV under toluene at  $18^{\circ}$ . This did not take place even after some days. Then we removed the toluene by washing with alcohol and ether, and put the salt under an aqueous, saturated solution of  $NH_4NO_3$ , with which it was left in contact at  $18^{\circ}$  for 24 hours. After drying for some days in vacuo, over sulphuric acid, and afterwards over  $P_2O_5$ , the density (originally  $1.647$ ) was again determined. It had remained unchanged.

When the salt had been once more under the aqueous solution for two days, the density had increased to  $1.677$  ( $1.677$ ); after having been under toluene for 24 hours, the salt showed a density of  $1.680$  ( $1.678$ ), three days and nights later  $1.680$  ( $1.678$ ).

Recapitulating we see that complete stabilization of modification III into IV at  $18^{\circ}$  did not take place, neither when it is in contact with a saturated aqueous solution, nor with the toluene or xylene preparations used.

<sup>1)</sup> These Proceedings 27, 65 (1924); Zeitschr. f. physik. Chemie 109, 81 (1924).

<sup>2)</sup> ERNST COHEN and A. L. TH. MOESVELD, Verslag etc. 28, 581, 602 (1920); Zeitschr. f. physik. Chemie 94, 471, 482 (1920).

*The caloric Measurements.*

15. For these measurements we have made use of the electrical, adiabatic calorimeter for the determination of heats of solution which was recently described by ERNST COHEN, A. L. TH. MOESVELD and W. D. HELDERMAN <sup>1)</sup>. For the experimental method and the calculation of the determinations we refer to the paper mentioned, reminding our readers that the accuracy of the determinations may be put at about 3 pro mille.

All the determinations made by us hold good for the temperature of the transition point of modification III into IV (32°.3 C).

16. Before giving the numerical results in table 2, we wish to make a remark about the preparation of the solutions, in which the intermediate heats of solution of the two modifications were determined, as well as about the way in which the flasks, containing the preparation to be solved, were prepared.

As ammonium nitrate is a hygroscopic substance, special precautions must be taken in weighing the salt which is put into the flasks, (up to the time of filling the flasks it had continually been kept over  $P_2O_5$ ). Our manner of procedure was as follows: in the afternoon the necessary quantities of salt were roughly weighed in the flasks as quickly as possible. Then they were placed again in the desiccator over  $P_2O_5$ , and the next day the weighings were done very accurately (flasks closed with stoppers). Then the flasks were sealed.

The flasks which contained modification III (metastable at room temperature) were always kept over  $P_2O_5$  at 60°, after the preliminary weighing had been done. After sealing, up to the moment when they were placed in the calorimeter, they were also kept at that temperature.

17. The stock of the solutions was prepared by weighing salt and water on a large balance, which could bear about 20 Kgm. Duplicate estimations were always made of the concentrations by determining the density of the solution. For this we used the equation we gave some time ago for the relation between concentration and specific volume of ammonium nitrate solutions at 32°.3<sup>2)</sup>). The solutions which were supersaturated at room temperature were kept in flasks standing in a thermostat which was kept at about 30°. Before transferring them to the calorimeter we warmed the solutions up to about 32°, and by means of the heating-stirrer we then raised the temperature to the temperature of the experiment (32°.3). All the weighings were reduced to vacuo.

18. Table II gives a survey of the calorimetric determinations.

<sup>1)</sup> These Proceedings 27, 656 (1924).

<sup>2)</sup> ERNST COHEN, W. D. HELDERMAN and A. L. TH. MOESVELD, These Proceedings 27, 565 (1924).

TABLE II.

Intermediate heats of solution of ammonium nitrate modification IV and III in solutions of ammonium nitrate concentration. Temp. 32° 3 C. (transition temperature).

Name of the modification.	Weight of the solution in gm.	Weight of the salt in gm.	Correction for Radiation in degrees Celsius	Initial concentration in gm. per 100 gm. solution	Final concentration in gm. per 100 gm. solution	Mean concentration in gm. per 100 gm. solution.	Intermediate heat of solution in gm. calories per mole.	Intermediate heat of solution in gm. cal. per mole corrected	Mean interm. heat of sol. in gm. calories per mole found.	Interm. heat of sol. in gm. cal. per mole calculated	Interm. heat of sol. in gm. cal. per mole calc.—found.
IV	1125.0	33.4363	-0.001	12.52	15.04	13.78	-4901	-4899			
IV	1120.5	33.3132	+0.000 <sup>b</sup>	12.55	15.08	13.81	-4909	-4906	-4903	-4902	+ 1
IV	1157.3	33.4923	±0.000	12.52	14.98	13.75	-4904	-4904			
III	1138.7	33.2520	-0.000 <sup>c</sup>	12.52	14.98	13.75	-4512	-4512			
III	1138.7	33.2558	-0.001	12.52	14.98	13.75	-4505	-4505	-4509	-4502	+ 7
IV	1212.0	32.8705	±0.000	26.53	28.47	27.50	-4123	-4123			
IV	1216.5	32.9919	+0.001	26.53	28.47	27.50	-4116	-4116	-4120	-4125	- 5
III	1171.1	33.0090	+0.001	26.47	28.49	27.48	-3715	-3716			
III	1128.4	32.8477	-0.001	26.46	28.54	27.50	-3718	-3718	-3717	-3725	- 8
IV	1240.9	43.8249	±0.000	40.30	42.34	41.32	-3581	-3579			
IV	1246.1	43.7685	-0.003	40.35	42.39	41.37	-3587	-3583	-3584	-3577	+ 7
IV	1288.1	43.0269	+0.003	40.29	42.22	41.25	-3589	-3589			
III	1313.0	43.6582	-0.001	40.29	42.22	41.25	-3190	-3190			
III	1287.1	43.2247	+0.000 <sup>b</sup>	40.28	42.22	41.25	-3183	-3183	-3187	3177	+10
IV	1315.7	41.3644	-0.001	54.07	55.47	54.77	-3200	-3200			
IV	1322.1	41.5644	-0.000 <sup>b</sup>	54.07	55.47	54.77	-3199	-3199	-3200	-3197	+ 3
III	1301.4	40.9142	-0.001	54.07	55.47	54.77	-2799	-2799			
III	1321.0	41.5153	+0.002 <sup>b</sup>	54.07	55.47	54.77	-2792	-2792	-2796	-2797	- 1
IV	1401.4	31.7401	+0.002	68.40	69.10	68.75	-2935	-2935			
IV	1398.6	31.6687	+0.001 <sup>a</sup>	68.40	69.10	68.75	-2944	-2944	-2940	-2945	- 5
III	1420.0	32.1607	+0.002	68.40	69.10	68.75	-2540	-2540			
III	1407.1	31.8874	±0.000	68.40	69.10	68.75	-2538	-2538	-2539	-2545	- 6

It is to be noted that the figures of the ninth column were obtained by converting the values of the eighth column to the same mean concentration in so far these concentrations were not equal.

19. As the absolute value of the heats of solution measured depends on the value of the E. M. F. of the WESTON-cell at 25° 0 C. we have, during the investigation, continually compared the E. M. F. of the two WESTON-standards used with that of a CLARK-cell, which was placed in the same thermostat as the WESTON-cell at 25° 0 C. We found:

Date	$\left(\frac{\text{E.M.F. CLARK}}{\text{E.M. WESTON}}\right)_{25^{\circ}0}$
2 April 1924	1.3947
11 " "	1.3947
17 " "	1.3946
25 " "	1.3947
5 May "	1.3947
17 " "	1.3948
26 " "	1.3947
2 June "	1.3948
13 " "	1.3948

20. In connexion with the investigations of ERNST COHEN and A. L. TH. MOESVELD on the intermediate heats of solution of *m.* dinitro benzene in ethylacetate<sup>1)</sup>, we have first of all tried to represent the relation between the intermediate heats of solution ( $Q_i$ ) and the mean concentration ( $c$ ) of the solutions of ammonium nitrate by means of a quadratic equation of the form:

$$Q_i = A + B(1 - c)^2,$$

in which  $A$  and  $B$  are constants,  $c$  the concentration expressed in gm. of salt per 100 gm. of solution. As this equation did not hold<sup>2)</sup> along the great concentration interval which was investigated by us, we have tried an equation of the third degree, computed by the method of least squares.

For modification IV it runs:

$$(Q_i)_{IV} = -5910 + 83.057 c - 0.73476 c^2 + 0.00224 c^3 \quad \dots (1),$$

for modification III:

$$(Q_i)_{III} = -5510 + 83.057 c_1 - 0.73476 c_1^2 + 0.00224 c_1^3 \quad \dots (2)$$

<sup>1)</sup> Verslag etc. 26, 1553 (1918); Zeitschr. f. physik. Chemie 93, 385 (1919).

<sup>2)</sup> According to this equation:

$$(Q_i)_{IV} = -5822 + 73.697 c - 0.4649 c^2$$

and

$$(Q_i)_{III} = -5422 + 73.697 c_1 - 0.4649 c_1^2,$$

we find divergencies between the values calculated and found as high as 0.8 per cent.

From column 11 and 12 in Table II we see, that these equations satisfy the determinations.

21. If in (2) we put  $c_1 = c$ , we find for the heat of transition III  $\rightarrow$  IV (at 32°.3 C.):

$$W = (Q)_{III} - (Q)_{IV} = -5510 + 5910 = \\ = +400 \frac{\text{gm. calories}}{\text{mol.}} = +4.99 \frac{\text{gm. calories}}{\text{gm.}}$$

BRIDGMAN (see par. 1) has found for it

$$4.66 \frac{\text{gm. calories}}{\text{gm.}}$$

As was to be expected according to our determinations of  $(v_{III} - v_{IV})$  at 32°.3 we find in the caloric figure of BRIDGMAN an error of about the same magnitude as in his figure of volume measurements. It may be expected, and this was already pointed out in par. 1, that his determination of  $\frac{dT}{dp}$  does not contain grave errors, because, owing to his method of procedure, the presence of metastable mixtures does not play a role here.

22. Finally a single remark on other investigations concerning the transformation of ammonium nitrate III into IV.

To an accidental compensation of errors must, in view of the facts mentioned above (par. 2 and 3), be attributed that BELLATI and ROMANESE have found a value for the heat of transition which is in close agreement to our figure. In this connexion we call attention to what ERNST COHEN and A. L. TH. MOESVELD <sup>1)</sup> communicated about the experimental testing of BRAUN'S Law, in which investigation they proved that SILL'S <sup>2)</sup> results agreed with the equation mentioned to within a few per cents, notwithstanding the errors up to 20 per cent in his measurements.

We need not discuss here the determinations of TAMMANN <sup>3)</sup> and of LUSSANA <sup>4)</sup> as they lie outside the scope of these investigations, especially because an accurate measurement of pressure is wanting.

## SUMMARY.

Intermediate heats of solution of the modifications III and IV of ammonium nitrate were determined at the transition temperature (32°.3 C.)

<sup>1)</sup> Verslag etc. 26, 1241 (1918); Zeitschr. f. physik. Chemie 93, 385 (1919).

<sup>2)</sup> Journ. Americ. Chem. Soc. 38, 2632 (1916).

<sup>3)</sup> Kristallisieren und Schmelzen, Leipzig 1903, Page 299 et seq.

<sup>4)</sup> Il Nuovo Cimento (4) 1, 97 (1895).

by an adiabatic, electrical method. From these the heat of transition of this transformation was calculated. It was shown to be  $4.99 \frac{\text{gm. cal.}}{\text{gm.}}$ . As was to be expected, the value which BRIDGMAN found for it ( $4.66 \frac{\text{gm. cal.}}{\text{gm.}}$ ) is erroneous, as is also his determination of the change of volume at the transition temperature, in consequence of the fact that he experimented with a metastable mixture instead of with the pure modifications.

We beg to express our best thanks to Mr. H. G. S. SNIJDER, chem. docts., who very kindly assisted us in carrying out the caloric measurements.

*Utrecht, June 1924.*

VAN 'T HOFF-Laboratory.

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**Mathematics.** — "*The Rank-Numbers of an Involution of Rays in Space*". By Dr. G. SCHAAKE. (Communicated by Prof. HENDRIK DE VRIES).

(Communicated at the meeting of October 25, 1924).

§ 1. Whereas involutions of groups of points in the plane or in space have already been investigated extensively a long time ago, the involutions of rays in space have only recently drawn the attention, except the involutions of the pairs of associated directrices of a linear complex and of the pairs of mutual polar lines of a quadratic surface. Prof. JAN DE VRIES has indicated and investigated several of those involutions <sup>1)</sup> and Prof. C. H. VAN OS has treated another <sup>2)</sup>.

For the investigation of the involutions of points in the plane the introduction of the rank-number, which indicates how many pairs of points of such an involution lie on an arbitrary straight line, has been of great importance. If  $r$  is this rank-number for an involution of pairs of points of the order  $n$  in the plane, this involution has a curve of double points of the order  $n-2r$ . BERTINI <sup>3)</sup>, MARTINETTI <sup>4)</sup> and BERZOLARI <sup>5)</sup> have determined the involutions of pairs of points for which the value of this rank-number is from one to five. The involutions of point-triples for which this rank-number is one, have been investigated by Prof. JAN DE VRIES <sup>6)</sup>.

In the following paper we shall show that to an involution of rays of which two conjugated lines cross each other as a rule, there belong *three* rank-numbers. After that we shall derive some relations existing between these rank-numbers, the order of the complex of the double-lines and a few other numbers that are characteristic for the involution of rays. Finally we shall try to find which are the involutions of rays of which the rank-numbers have the values zero or one.

§ 2. If we represent the rays of space in the well-known way on the points of a four-dimensional quadratic variety  $V_4$ , lying in a five-

<sup>1)</sup> These Proceedings, 22, 478, 482, 634; 23, 462, 466; 22, 493; Revista Matematica, t. 5, p. 65. A paper of the author in these Proceedings, 22, 488 deals also with the involution of rays of the first mentioned paper.

<sup>2)</sup> These Proceedings 22, 580.

<sup>3)</sup> Lomb. Ist. Rend., ser. 2, vol. 16, p. 89 and 190.

<sup>4)</sup> Annali di Mat., ser. 2, t. 12, p. 73, and ser. 2, t. 13, p. 53.

<sup>5)</sup> Annali di Mat., ser. 2, t. 16, p. 191.

<sup>6)</sup> These Proceedings, 16, 974 and 21, 291. Involutions of groups of  $n$  points have been treated by FERRETTI. Rend. di Palermo, t. 17, p. 311.

dimensional space  $R_5$ , an involution formed by pairs of lines in space which cross each other as a rule, is transformed into an involution of pairs of points of  $V_4$  the carriers of which generally do not lie on  $V_4$ . These carriers form a system of  $\infty^4$  straight lines of  $R_5$ .

Now such a system  $S_4$  has three characteristic numbers <sup>1)</sup>. The first indicates the number of straight lines of  $S_4$  through a given point of  $R_5$ ; the second the number of straight lines of  $S_4$  lying in an  $R_4$  belonging to  $R_5$  which intersect a straight line of the above mentioned  $R_4$ , and the third the number of straight lines of  $S_4$  in an  $R_3$  of  $R_5$ . In accordance with the definition of the rank of an involution of pairs of points in the plane given in § 1, according to which this rank is equal to the characteristic number of the system of  $\infty^2$  joins of the pairs of points, we introduce as rank-numbers of an involution  $I$  of pairs of lines which as a rule cross each other, the three characteristic numbers of the system of  $\infty^4$  lines joining the pairs of points of  $V_4$  on which the pairs of rays of  $I$  are represented.

The three rank-numbers  $r_1$ ,  $r_2$  and  $r_3$  of the involution of rays indicate therefore resp.:

1. the number of pairs of  $I$  consisting of straight lines which are conjugated to each other relative to a given linear complex;
2. the number of pairs of  $I$  lying in a given linear complex  $C$  that belong to the same scroll with two straight lines given in  $C$ ;
3. the number of pairs of  $I$  that belong to a given bilinear congruence of rays.

§ 3. An involution of rays  $I$  of which the first rank-number is  $r_1$ , contains  $r_1$  pairs of which the straight lines are conjugated to each other relative to a given linear complex  $C$ . If we take for  $C$  a special linear complex with axis  $a$ , a pair of conjugated directrices of  $C$  consists of  $a$  and an arbitrary line or of two straight lines lying in a plane pencil together with  $a$ .

*The first rank-number of an involution of rays  $I$  is therefore equal to the sum of the two numbers which indicate resp. how many lines of  $I$  are conjugated to an arbitrary straight line and how many pairs of  $I$  belong to one plane pencil together with an arbitrary straight line.*

$I$  contains  $\infty^3$  pairs of rays of which the lines cut each other. If we conjugate the point of intersection of each such a pair to its plane, there generally arises a null system  $N(a, \beta, \gamma)$ .

*For the third characteristic number of this null system, which indicates how many times a point  $P$  lies on a given straight line  $l$  while the plane  $\pi$  corresponding in  $N$  to  $P$  passes through  $l$ , we have therefore the equation:*

$$\gamma = r_1 - m \dots \dots \dots (1)$$

<sup>1)</sup> See e.g. § 5 of my paper "A new Method for the Solution of the Problem of the Characteristics in the enumerative Geometry," These Proceedings 25, 113.

if  $m$  represents the number of straight lines which are conjugated in  $I$  to a given straight line.

The second rank-number  $r_2$  of  $I$  indicates how many pairs of  $I$  lie in a given linear complex  $C$  and belong to one scroll together with two straight lines  $c_1$  and  $c_2$  given in  $C$ . If for  $c_1$  and  $c_2$  we choose two lines of  $C$  cutting each other, a scroll containing  $c_1$  and  $c_2$  always degenerates into the plane pencil  $(c_1, c_2)$  and another plane pencil  $w$  of which the vertex lies in the plane through  $c_1$  and  $c_2$  and the plane passes through the point of intersection of  $c_1$  and  $c_2$ . If  $(c_1, c_2)$  is chosen arbitrarily, there are apparently no two straight lines conjugated to each other in  $I$  which lie in this plane pencil. If  $n$  is the order of the scroll corresponding in  $I$  to an arbitrary plane pencil,  $C$  has  $n$  straight lines in common with the scroll conjugated to  $(c_1, c_2)$ . If further  $\varepsilon$  is the order of the complex of the double lines of  $I$ , the number  $n-\varepsilon$  of the pairs of  $I$  belonging to  $C$  of which one straight line lies in  $(c_1, c_2)$ , is included in  $r_2$ . We exclude the  $\varepsilon$  double rays of  $I$  in  $(c_1, c_2)$  through which the scroll corresponding to  $(c_1, c_2)$  also passes, because as a rule the carriers of the coincidences of the point-involution on  $V_4$  representing  $I$ , which correspond to these double rays, do not lie in the  $R_4$  which is conjugated to  $C$ .

$r_2$  includes also the number of the pairs of rays of  $I$  in plane pencils of  $C$  the vertices of which lie in the plane through  $c_1$  and  $c_2$  and the planes of which pass through the point of intersection of these lines. The plane pencils of  $C$  satisfying these two conditions, form a pencil of  $\infty^2$  individuals for which the three characteristic numbers are equal to one. For the characteristic numbers of such a system indicate the order of the surface of the vertices, the class of the envelope of the planes, and the number of plane pencils of which the planes pass through a given point and the vertices lie in a given plane. This system has  $a + \beta + \gamma$  individuals in common with the system  $(a, \beta, \gamma)$  of  $\infty^3$  plane pencils containing two intersecting rays of  $I$ <sup>1)</sup>.

Hence:

$$r_2 = n - \varepsilon + a + \beta + \gamma \dots \dots \dots (2)$$

The order of the complex of the double lines of an involution of rays is accordingly equal to:

$$n - r_2 + a + \beta + \gamma.$$

Finally we treat in the same way the third rank-number  $r_3$  of  $I$ , which indicates how many pairs of rays of  $I$  belong to a given linear congruence. We choose a bilinear congruence of which the directrices cut each other and which is accordingly formed by all the straight lines passing through the point of intersection  $P$  of the directrices or lying in the plane  $\pi$  of these lines. We see in this case that  $r_3$  contains in the

<sup>1)</sup> See e.g. my thesis for the doctorate: "Afbeeldingen van figuren op de punten eener lineaire ruimte", Groningen 1922, p. 112.

first place the numbers  $\alpha$  and  $\beta$  of the pairs of  $I$  of which the lines resp. cut each other in  $P$  or lie in  $\pi$ . If  $p$  is the number of pairs of  $I$  of which one line passes through a given point and the other lies in given plane,  $r_3$  contains also the number  $p-\varepsilon$  of the pairs of  $I$  of which one line passes through  $P$  and the other lies in  $\pi$ . We exclude the  $\varepsilon$  coincidences of  $I$  in the plane pencil  $(P, \pi)$ , because the carriers of the corresponding coincidences of the point-involution conjugated to  $I$  on  $V_4$ , do not lie in the  $R_3$  which contains the image of the chosen degenerate bilinear congruence.

We find accordingly for  $r_3$ :

$$r_3 = p - \varepsilon + \alpha + \beta \dots \dots \dots (3)$$

so that the order of the complex of the double lines of  $I$  may also be written:

$$p - r_3 + \alpha + \beta.$$

By the aid of (1) and (2) we arrive at the following relation, which exists between  $m, n, p$  and the rank-numbers of  $I$ :

$$r_1 - r_2 + r_3 = m - n + p \dots \dots \dots (4)$$

We find a formula containing another number remarkable for  $I$ , if we consider the correspondence which arises if we conjugate to each line  $l$  of a given plane pencil the line  $l''$  of the same pencil which cuts a line  $l'$  associated to  $l$  in  $I$ . In this correspondence apparently  $m$  lines  $l'$  are associated to a line  $l$ . As besides  $\varepsilon$  generatrices the scroll corresponding to the plane pencil has a curve of the order  $n-\varepsilon$  in common with the plane of the pencil, a ray  $l''$  cuts  $n-\varepsilon$  more lines  $l'$  and consequently  $n-\varepsilon$  lines  $l$  correspond to a line  $l''$ . Accordingly the correspondence  $(l, l')$  has  $m + n - \varepsilon$  coincidences. These lie in the first place in the  $\varepsilon$  double rays of  $I$  in the given plane pencil and further in the  $\sigma$  generatrices each of which is cut by a line conjugated to it in  $I$ . The number of the latter generatrices may therefore be found by the formula:

$$\sigma = m + n - 2\varepsilon^1) \dots \dots \dots (5)$$

The number  $\sigma$  may also be considered as the order of the complex of the lines that are cut by the lines which are conjugated to them in  $I$ .

We remark that the formulas derived in this §, cannot be applied to an involution of rays which only consists of pairs of intersecting lines. For if in this case we conjugate to each other the point of intersection and the plane of any such a pair of lines, we do not get a null-system but a system of  $\infty^4$  plane-elements and accordingly  $\alpha, \beta$  and  $\gamma$  as well as  $\sigma$  become infinite.

The considerations of § 1—§ 3 hold also good if instead of an involution we take an involutorial correspondence in the rays of space.

§ 4. From formula (1) of § 3 there follows that the first rank-number of an involution of rays  $I$  in which to each straight line of space one or more straight lines are conjugated, is at least one. This appears also

<sup>1)</sup> Cf. SCHUBERT, Kalkül der Abzählenden Geometrie, p. 58, (5).

in the following way. If the first rank-number is zero, no straight line of the system  $S_4$  of  $\infty^1$  rays corresponding to  $I$  passes through an arbitrary point of  $R_5$ . The lines of  $S_4$  form a variety which does not coincide with  $V_4$ , because in that case all the pairs of  $I$  would consist of lines which cut each other. Accordingly straight lines of  $S_4$  pass only through those points of  $V_4$  which lie on the intersection of  $V_4$  and the variety containing  $S_4$ , so that no line in  $I$  corresponds to a line of which the image point does not lie on this intersection.

We shall therefore investigate only those involutions of rays for which the first rank-number is one.

If the three rank-numbers are one, zero and zero, the carriers of the pairs of the point-involution on  $V_4$  corresponding to  $I$ , form a system  $S_4$  (1,0,0) of  $\infty^1$  straight lines of  $R_5$ . According to § 2 an arbitrary  $R_3$  does not contain any line of  $S_4$ , nor does an arbitrary  $R_4$  contain a straight line which cuts another straight line chosen arbitrarily in this  $R_4$ . Hence an arbitrary  $R_4$  does not contain any line of  $S_4$ . For the lines of  $S_4$  in an  $R_4$  would form one or more surfaces each containing  $\infty^2$  straight lines, as a line of  $R_4$  which cuts one line of  $S_4$  in this space, must cut an infinite number of them, for which reason an  $R_4$  cannot contain a system of  $\infty^1$  or a finite number of lines of  $S_4$ . This surface would necessarily be formed by one or more planes, which is in contradiction to the fact that an  $R_3$ , through which we can always pass an  $R_4$ , does not contain any line of  $S_4$ .

The four-dimensional spaces  $R_4^1$  which contain straight lines of  $S_4$ , form therefore a special system. One of the individuals of this system passes through a given  $R_3$ . For the rays of  $S_4$  cutting an  $R_3$ , form a variety which has in common with an  $R_4$  through this  $R_3$  the latter space, because, as appears from the first characteristic number of  $S_4$ , through any point of the  $R_3$  there passes a line of  $S_4$ . As the  $R_4$  mentioned does not generally contain any line of  $S_4$ , the lines of  $S_4$  which cut an  $R_3$ , lie in a linear four-dimensional space, the only  $R_4$  which may be passed through this  $R_3$  in which there lie lines of  $S_4$ . The spaces  $R_4$  are accordingly the four-dimensional spaces that pass through a point  $S$  of  $R_5$  and the rays of  $S_4$  are the lines through  $S$ . Two points of  $V_4$  on the same line of  $S_4$  represent two rays which are conjugated to each other relative to the linear complex corresponding to the intersection of  $V_4$  with the polar space of  $S$  relative to  $V_4$ .

*Consequently an involution of rays with rank-numbers one, zero and zero is always formed by the pairs of lines which are conjugated to each other relative to a linear complex.*

For such an involution  $m = n = p = \varepsilon = 1$  and  $\alpha = \beta = \gamma = \sigma = 0$ . These numbers satisfy the five formulas found in § 3.

To an involution of rays for which the rank-numbers are one, zero and one, there corresponds on  $V_4$  an involution of pairs of points the carriers of which form a system  $S_4$  (1, 0, 1) of  $\infty^1$  rays of  $R_5$ . In this

case the lines of  $S_4$  which belong to an  $R_4$ , are the rays of a congruence  $(0,1)$ , that is a system of  $\infty^2$  straight lines none of which cuts a line given in this  $R_4$  and one of which belongs to an  $R_3$  given in the  $R_4$ . Accordingly the lines of this congruence form a surface which must be one plane  $V$ , because any line of the  $R_4$  passing through a point of this surface, must cut an infinite number of lines of the congruence and an  $R_3$  of the  $R_4$  contains one line of the congruence. As through a plane there pass  $\infty^2$  four-dimensional spaces, there are  $\infty^3$  planes  $V$ .

Now through an arbitrary point of  $R_5$  there passes only one line of  $S_4$ . Hence all the straight lines of  $S_4$  cannot lie in planes  $V$ .

We consider two planes  $V$ , which we call  $V_1$  and  $V_2$ . They have one line in common, viz. the line of  $S_4$  lying in the  $R_3$  which belongs to an  $R_4$  through  $V_1$  and an  $R_4$  through  $V_2$ . In the same way the plane  $V$  of an arbitrary  $R_4$  has one line in common with each of the planes  $V_1$  and  $V_2$  and it belongs therefore to the  $R_3$  which is defined by  $V_1$  and  $V_2$ . Consequently the system  $S_4$  degenerates into that of the lines of the latter three-dimensional space  $R_3^1$  and a system with rank-numbers one, zero and zero which is formed by the lines of  $R_5$  passing through a definite point. Accordingly the involution of rays consists of the  $\infty^4$  pairs of straight lines that are conjugated to each other relative to a linear complex, and of the  $\infty^4$  pairs of rays of the bilinear congruence that are represented on the intersection of  $R_3^1$  and  $V_4$ .

*There is no non-degenerate involution of rays of which the rank-numbers are one, zero and one.*

§ 5. Now we shall investigate the involution of rays for which the three rank-numbers are one, one and zero, which is represented on a point-involution of  $V_4$  of which the system of carriers is a system  $S_4$   $(1,1,0)$  of  $\infty^4$  lines in  $R_5$ . The locus of the  $\infty^2$  rays of  $S_4$  lying in a four-dimensional space  $R_4$  of  $R_5$ , one of which cuts a line given in  $R_4$  as appears from the second rank-number of  $S_4$ , is a linear three-dimensional space  $R_3^1$ . In an arbitrary  $R_3$  of  $R_4$  there lies no line of  $S_4$ , hence neither in the plane of intersection of this  $R_3$  and the space  $R_3^1$  that corresponds to  $R_4$ . The lines of  $R_3^1$  which belong to an  $R_4$ , form therefore a congruence  $(1,0)$ , that is a sheaf of rays, of a three-dimensional space  $R_3^1$  of this  $R_4$ .

If an  $R_4$  describes a pencil of spaces, the locus of the vertices of the sheaves of rays of  $S_4$  which lie in the spaces of this pencil, has no point in common with the three-dimensional space of the axes, because the sheaf of rays of  $S_4$  which has such a point as vertex, would have a straight line [in the space of the axes and this space generally does not contain any line of  $S_4$ . The locus of the vertices of the sheaves of  $S_4$  in the spaces of the pencil under consideration has outside the space of the axes one point in common with each of its individuals and it is therefore a line  $a$ .

An arbitrary  $R_4$  cuts  $a$  in a point  $A$  and has in common with the  $R_4$  that belongs to the above mentioned pencil and passes through  $A$ , a plane pencil that has  $A$  as vertex and the plane of which is the intersection of the former  $R_4$  and the  $R_3^1$  of the latter  $R_4$ . Hence the vertex of the sheaf of rays of  $S_4$  that lies in an arbitrary  $R_4$ , always belongs to  $a$  and all the lines of  $S_4$  cut the line  $a$ . As an  $R_4$  through a point  $A$  of  $a$  has a sheaf of rays in a three-dimensional space in common with the locus of the lines of  $S_4$  through  $A$ , this locus is a linear four-dimensional space through  $A$ .

Accordingly to each point  $A$  of  $a$  there corresponds a four-dimensional space  $R_4^1$  so that the lines of this space through  $A$  are the rays of  $S_4$  through  $A$ . There are  $\infty^1$  spaces  $R_4^1$ , one of which passes through an arbitrary point  $P$  of  $R_5$ , namely the  $R_4^1$  that is conjugated to the point of  $a$  where the line of  $S_4$  through  $P$  cuts  $a$ . The spaces  $R_4^1$  form therefore a pencil that has a three-dimensional space  $I'$  as space of the axes; hence all the lines of  $S_4$  cut also  $I'$ .

Now the lines of intersection of  $a$  and  $I'$  form just such a system  $S_4(1, 1, 0)$ . Any line cutting  $a$  and  $I'$  must also belong to the chosen system  $S_4$  because it is the only line cutting  $a$  and  $I'$  which passes through one of its points outside  $a$  and  $I'$ .

*A system  $S_4(1, 1, 0)$  of  $\infty^4$  rays of  $R_5$  consists therefore of the lines which cut a given line  $a$  and a likewise given linear three-dimensional space  $I'$ ).*

The point  $L'$  corresponding to a given point  $L$  of  $V_4$  in the point-involution defined on this variety by  $S_4$ , is the second point of intersection of  $V_4$  with the line of intersection through  $L$  of the plane  $(L, a)$  and the four-dimensional space  $(L, I')$ . To the planes through  $a$  there correspond in the rays of space the scrolls containing the two lines  $m$  and  $n$  the images of which are the points of intersection of  $a$  and  $V_4$  and to the four-dimensional spaces through  $I'$  there correspond the linear complexes containing the bilinear congruence which is represented on the intersection of  $I'$  with  $V_4$ .

*An involution of rays for which the three rank-numbers are one, one and zero, is accordingly defined by two given straight lines  $m$  and  $n$  and a given bilinear congruence  $K$ . The line  $l'$  conjugated to a line  $l$ , is the line different from  $l$  which has the scroll  $(l, m, n)$  in common with the linear complex containing  $l$  and  $K$ .*

By the aid of a representation of the rays of space on a linear four-dimensional space of points, this involution has been treated in p. 84—92 of the thesis for the doctorate to which we referred in the foot-note to § 3.

To a plane pencil, a sheaf, and a field of lines  $l$  there are resp. conjugated a cubic scroll, a congruence  $(1, 2)$  and a congruence  $(2, 1)$  of lines

<sup>1)</sup>  $a$  can be infinitely near to  $I'$ .

$l'$ . Hence the numbers  $m$ ,  $n$  and  $p$  of § 3 are resp. 1, 3 and 2 so that the relation (4) of § 3 is satisfied.

As this involution of rays has a quadratic complex of double lines, there results from the formulas (1), (2), (3) and (5) of § 3 that  $\alpha = \beta = \gamma = \sigma = 0$ . The  $\infty^3$  pairs of rays  $(l, l')$  for which  $l$  and  $l'$  cut each other, are in fact the pairs of generatrices of the plane pencils that contain  $m$  or  $n$  and a line of  $K$ , and these pairs  $(l, l')$  define only  $\infty^1$  plane-elements; the lines  $l$  that are cut by the conjugated line  $l'$ , form no complex but two special bilinear congruences.

§ 6. Finally we determine the involution of rays for which each of the three rank-numbers is one. Such an involution  $I$  is represented on a point-involution of  $V$  of which the carriers of the pairs of points form a system  $S_4(1, 1, 1)$  of  $\infty^4$  lines in  $R_5$ . According to § 2 one line  $d$  of  $S_4$  passes through a given point  $P$  of  $R_5$ . The rays of  $S_4$  which lie in an  $R_4$ , are the lines of a system of  $\infty^2$  lines one of which cuts a given straight line of this  $R_4$ ; they form therefore a linear three-dimensional space  $R_3^1$ . An arbitrary three-dimensional space  $R_3$  of the chosen  $R_4$  contains one line of  $S_4$ , which must lie in the plane of intersection of  $R_3$  and  $R_3^1$ .

Hence we see that an  $R_4$  contains a bilinear congruence of  $S_4$  lying in a three-dimensional space  $R_3^1$  that belongs to the  $R_4$  <sup>1)</sup>.

As each  $R_4$  contains one  $R_3^1$ , but each  $R_3^1$  is conjugated to the  $\infty^1$  spaces  $R_4$  passing through it, there are  $\infty^1$  spaces  $R_3^1$  each of which contains a bilinear congruence of  $S_4$ . The three-dimensional space through two crossing lines  $d$  of  $S_4$  contains more than one, hence an infinite number of lines of  $S_4$  and must be conjugated as  $R_3^1$  to each four-dimensional space passing through it. If two spaces  $R_3^1$  have only one line in common, this is a generatrix of  $S_4$ . For if we pass an  $R_3$  through each of these spaces, they have an  $R_3$  in common and the line of  $S_4$  belonging to this  $R_3$ , must necessarily be the line of intersection mentioned.

We choose a space  $R_3^1$ , which we call  $\Delta$ , and a straight line  $d_1$  of  $S_4$  which does not cut  $R_3^1$ . In order to do this we have only to start from an arbitrary  $R_4$  and to choose the  $R_3^1$  belonging to it with the line  $d_1$  of  $S_4$  through an arbitrary point of the  $R_4$  outside this  $R_3^1$ . A space  $R_3^1$  through  $d_1$  cuts  $\Delta$  along a line of the bilinear congruence  $C_1$  of  $S_4$  lying in  $\Delta$ . Inversely an  $R_3$  through  $d_1$  and a straight line of  $C_1$  is a space  $R_3^1$ . Hence the projection of  $S_4$  out of  $d_1$  on  $\Delta$  is  $C_1$ , the same as that of a bilinear congruence of  $C$  of  $S_4$  which lies in a space  $R_3^1$  that does not pass through  $d_1$ .

If  $\delta_1$  and  $\delta_2$  are the directrices of  $C$ , one of the directrices of each

<sup>1)</sup> If the lines of an  $R_4$  always formed a sheaf of rays in an  $R_3$  and a field,  $S_4$  would degenerate into a system (1,1,0) and a system (0,0,1).

congruence  $C$  lies in the three-dimensional space  $(d_1, \delta_1)$ , the other in  $(d_2, \delta_2)$ . One directrix of  $C$  must apparently lie in both the spaces  $(d_1, \delta_1)$  and  $(d_2, \delta_2)$ , which, as they do not coincide and contain moreover both the line  $\delta_1$ , have a plane  $V_1$  in common in which each congruence  $C$  has one of its directrices. In the same way it appears that the other directrix of each congruence  $C$  lies in a plane  $V_2$  which the spaces  $(d_1, \delta_2)$  and  $(d_2, \delta_2)$  have in common.

Accordingly the directrices of  $S_4$  must cut the two planes  $V_1$  and  $V_2$ . Now the straight lines which cut two planes  $V_1$  and  $V_2$  chosen at random in  $R_5$ , form a system  $S_4(1, 1, 1)$ . Each line cutting  $V_1$  and  $V_2$  must also belong to the chosen system  $S_4$ , because it is the only line cutting  $V_1$  and  $V_2$  which passes through one of its points outside  $V_1$  and  $V_2$ .

*Consequently a system of  $\infty^3$  rays in  $R_5$  of which the three characteristic numbers are one, always consists of the lines which cut two given planes<sup>1)</sup>.*

We find the point  $L^1$  corresponding to a given point  $L$  of  $V_4$  in the point-involution on this variety where the lines of  $S_4$  are the carriers of the pairs of points, if we form the three-dimensional spaces  $(L, V_1)$  and  $(L, V_2)$  and determine the second point of intersection with  $V_4$  of the line of intersection of these spaces. To  $V_1$  and  $V_2$  there correspond in the rays of space resp. the scrolls  $\varphi_1$  and  $\varphi_2$ . In order to find the ray  $l'$  which corresponds in the involution in question to a given line  $l$ , we must therefore form the two bilinear congruences  $(l, \varphi_1)$  and  $(l, \varphi_2)$ .  $l'$  is the line which these congruences have in common besides  $l$ . The pairs of directrices of  $(l, \varphi_1)$  and  $(l, \varphi_2)$  are resp. the pairs of generatrices of the scrolls  $\varrho_1$  and  $\varrho_2$  conjugated to  $\varphi_1$  and  $\varphi_2$  which cut  $l$ .

*Accordingly an involution of rays of which the three rank-numbers are one, always consists of the pairs of rays of which the lines  $l$  and  $l'$  cut the same generatrices of two given scrolls  $\varrho_1$  and  $\varrho_2$ .*

This involution has already been investigated by Prof. JAN DE VRIES<sup>2)</sup>.

To a plane pencil, a sheaf and a field of lines  $l$ , there correspond resp. a cubic scroll, a congruence (2, 3) and a congruence (3, 2) of lines  $l'$ . Hence the numbers  $m$ ,  $n$  and  $p$  of § 3 are resp. 1, 3 and 3. The relation (4) of § 3 is accordingly satisfied.

The formula (1) of § 3 gives that  $\gamma = 0$ . If we have two conjugated lines  $l$  and  $l'$  of the involution in question which cut each other, through the point of intersection there must pass a generatrix of  $\varrho_1$  and a generatrix of  $\varrho_2$  and the plane through  $l$  and  $l'$  must contain a line of each of these two scrolls. Hence the point of intersection of two such lines  $l$  and  $l'$  always lies on the curve of intersection  $k^4$  of the two quadratic surfaces formed by  $\varrho_1$  and  $\varrho_2$ , and the plane  $(l, l')$  is a common tangent

<sup>1)</sup>  $V_1$  and  $V_2$  can be infinitely near to each other.

<sup>2)</sup> These Proceedings 22, 634. By the aid of the representation of the rays of space on  $V_4$ , this involution has been treated by Mr. H. B. BONE, Wiskundige Opgaven, part 14, p. 150.

plane of them. Any point of  $k^4$  is the vertex of one plane pencil of which two arbitrary generatrices form a pair of the involution in question. Hence  $\alpha = \beta = \gamma = 0$ . As the lines  $l$  that are cut by the conjugated lines  $l'$ , form a congruence, of which an arbitrary plane pencil does not contain any line, also  $\sigma = 0$ . Now the formulas (2), (3) and (5) of § 3 give, that there exists a quadratic complex of double rays, which has indeed been found.

If  $V_1$  and  $V_2$  have a point in common, the same holds good for the planes  $W_1$  and  $W_2$  conjugated to them relative to  $V_4$ , and  $\varphi_1$  and  $\varphi_2$  lie in the linear complex  $K_\varphi$  that is conjugated to the space  $(V_1, V_2)$ , and  $\varrho_1$  and  $\varrho_2$  in the linear complex  $K_\varphi$  that corresponds to the space  $(W_1, W_2)$ . In this case the system  $S_4$  of the lines cutting  $V_1$  and  $V_2$  degenerates into the system of lines through the point of intersection of  $V_1$  and  $V_2$  and the system of lines of the four-dimensional space  $(V_1, V_2)$  which cuts the planes  $V_1$  and  $V_2$ . The rays of the latter system are the lines of the  $\infty^2$  planes which have a line in common with each of the planes  $V_1$  and  $V_2$  and they are accordingly the carriers of the pairs of points of the  $\infty^2$  conics of  $V_4$  that have two points in common with each of the conics along which  $V_4$  is intersected by  $V_1$  and  $V_2$ . The involution of rays corresponding to  $S_4$ , degenerates in this case into that of the pairs of rays which are conjugated to each other relative to  $K_\varphi$  and the system of the  $\infty^4$  pairs of rays of the  $\infty^2$  scrolls which contain two lines of each of the scrolls  $\varphi_1$  and  $\varphi_2$ . The rank-numbers of the latter system are zero, one and one.

If  $\varphi_1$  and  $\varphi_2$  are the scrolls of the same quadratic surface  $\Phi$  and accordingly  $\varrho_1$  and  $\varrho_2$  coincide resp. with  $\varphi_2$  and  $\varphi_1$ , the planes  $V_1$  and  $V_2$  are conjugated to each other relative to the variety  $V_4$ .  $I$  splits off from the system of the  $\infty^4$  pairs of lines which touch  $\Phi$  at the same point.

*The remaining involution, of which still all the rank-numbers are one, is the involution of the pairs of mutual polar lines of the quadratic surface  $\Phi$ .*

For this involution of rays  $m = n = p = 1$ . Further  $\alpha = \beta = \gamma = 0$ , because two intersecting straight lines are conjugated to each other if they belong to the same plane pencil of tangents to  $\Phi$  and if they separate harmonically the two lines of  $\Phi$  lying in this plane pencil. The formulas (1) and (4) of § 3 are therefore satisfied. There follows from (2) and (3) that  $\varepsilon = 0$ . There are in fact in this case only two scrolls of double lines. Further (5) gives that  $\sigma = 2$ . The lines in a plane pencil that are cut by the conjugated lines, are accordingly the tangents to  $\Phi$  lying in the plane pencil.

**Physics.** — “*Determinations of the Terms in the Lanthanum Spectrum*”<sup>1)</sup>.

By S. GOUDSMIT. (Communicated by Prof. P. EHRENFEST).

(Communicated at the meeting of October 25, 1924).

Most earlier measurements of the ZEEMAN effect in not classified spectra are insufficient to successfully apply LANDÉ's rules<sup>2)</sup> to them with a view to arrange the lines. An exception to this are the accurate measurements by S. RYBAR<sup>3)</sup> in the spectrum of Lanthanum.

In this same spectrum groups of lines with equal frequency differences have been found by E. PAULSON<sup>4)</sup>.

Starting from these investigations a number of lines could be arranged in a term system, the relative term values could be determined, and the corresponding “innere Quantenzahl”  $J$  and factor of resolution  $g$  could be found for every term. Of the groups of lines found by PAULSON only those have been taken which were sufficiently certain by the observed ZEEMAN effects. Also several other lines have been classified, which did not occur in PAULSON's groups of lines.

From the ZEEMAN resolutions it appeared first of all that all classified lines belong to odd term-systems, hence that according to KOSSEL and SOMMERFELD's law of displacement they all are due to the *ionized* Lanthanum atom.

When the “innere Quantenzahl”  $J$  and the resolution factor  $g$  of a term are known from the ZEEMAN effects, it is generally possible to determine also the quanta values  $K$  and  $R$  by the aid of LANDÉ's formulae or table, i.e. the term symbol  $s, p, d$  etc. and also the term system, doublet, triplet, etc. can be found.

For some terms found in the Lanthanum spectrum this does not apply, however. Evidently these are the terms “höherer Stufe” examined of late by LANDÉ and HEISENBERG<sup>5)</sup>. Of these terms the relation between  $g$  and the quanta values is not yet known, hence their term symbols could not be determined. They are indicated by Roman numerals in the tables.

Nor is it excluded that some of the ordinary terms of the first rank found are in reality terms of higher rank, which happen to have

1) Preliminary communication in *Die Naturwissenschaften*. 12, 851, 1924.

2) A. LANDÉ, *Zeitschr. f. Phys.* 15, 189, 1923.

3) S. RYBAR, *Diss. Budapest and Phys. Zeit.* 12, 889, 1911.

4) E. PAULSON, *Ann. der Phys.* 45, 1203, 1914.

5) W. HEISENBERG, *Zeitschr. f. Phys.* 26, 291, 1924. A. LANDÉ u. W. HEISENBERG, *Zeitschr. f. Phys.* 25, 279, 1924.

corresponding  $J$  and  $g$  values. This might e.g. be the case with the triplet terms  $\bar{d}_1$  and  $\bar{d}_2$ , as the corresponding term  $\bar{d}_3$  could not be found.

The occurrence of such terms of higher rank means, according to LANDÉ, that in the state in question the atom rest — i.e. the atom without the emitting electron — contains electron groups with azimuthal quanta values greater than 1, which do not form a closed configuration without moment of momentum. In the case of ionized Lanthanum this means very probably that the non-emitting electron of the two outer ones can sometimes describe a  $6p$ - and sometimes a  $5f$ -path. In the former case the ordinary terms are obtained, in the latter case those of higher rank.

TERM TABLE.

Relative value of the term	Term symbol	$J$	$g$
0	$p_1$	$2^{1/2}$	$3/2$
1043.4	$p_2$	$1^{1/2}$	$3/2$
1418.8	$p_3$	$1/2$	$0/0$
3705.8	I	$2^{1/2}$	$1.50 \pm 0.01$ (tripl. $p_1$ of quint. $d_3$ ?)
4888.7	$\bar{d}_1$	$3^{1/2}$	$4/3$
5049.5	II	$1^{1/2}$	$1.28 \pm 0.03$
5780.3	III	$1^{1/2}$	$0.87 \pm 0.01$
5815.8	$\bar{d}_2$	$2^{1/2}$	$7/6$
6790.1	IV	$2^{1/2}$	$0.84 \pm 0.04$
7231.0	V	$1^{1/2}$	$0.78 \pm 0.02$
8681.5	VI	$3^{1/2}$	$1.05 \pm 0.03$ (tripl. $t_2$ ?)
8741.4	VII	$2^{1/2}$	$0.88 \pm 0.04$
26975.5	$\bar{p}_1$	$2^{1/2}$	$3/2$
27484.7	$\bar{p}_2$	$1^{1/2}$	$3/2$
27953.1	$\bar{p}_3$	$1/2$	$0/0$
29952.4	$d_1$	$3^{1/2}$	$4/3$
30611.6	$d_2$	$2^{1/2}$	$7/6$
31308.6	$d_3$	$1^{1/2}$	$1/2$
31808.4	D	$2^{1/2}$	1
33202.8	VIII	$2^{1/2}$	$0.73 \pm 0.02$

THE COMBINATION  $p \bar{p}$ 

$\lambda$	I	$\nu_{vac.}$	ZEEMAN effect	
			observed	calculated
3855.10	3	25932.3	(0) 1.49	(0) 1.50
3835.29	5	26066.3	(0) 1.51	(0) 1.50
3780.85	3 <sub>r</sub>	26441.6	(0) 1.40	(0) 1.50
3715.03	3	26910.0	(0) 1.53	(0) 1.50
3706.02	5	26975.5	(0) 1.50	(0) 1.50
3637.35	3	27484.7	(0) 1.50	(0) 1.50

	$p_1 \ 2^{1/2}$		$p_2 \ 1^{1/2}$		$p_3 \ 1^{1/2}$
$\bar{p}_1 \ 2^{1/2}$	26975.5	<b>1043.2</b>	25932.3		
	<b>509.2</b>		<b>509.3</b>		
$\bar{p}_2 \ 1^{1/2}$	27484.7	<b>1043.1</b>	26441.6	<b>375.3</b>	26066.3
			<b>468.6</b>		
$\bar{p}_3 \ 1^{1/2}$			26910.0		

THE COMBINATION  $p d$ 

$\lambda$	I	$\nu_{vac.}$	ZEEMAN effect	
			observed	calculated
3381.10	10	29567.7	(0) (0.40) <b>0.82</b> 1.17 1.59	(0) (0.33) <b>0.83</b> 1.17 1.50
3344.71	7	29889.4	(0) 0.52	(0) 0.50
3337.67	15	29952.4	(0) 1.13	(0) <b>1.00</b> 1.17 1.33.....
3303.26	5	30264.4	0.52 (1.00) 1.53	(0.50) (1.00) 1.53
3265.79	4	30611.6	(0.67) 0.76 <b>1.15 1.59</b> 1.97	(0.67) 0.83 <b>1.17 1.50</b> 1.83
3193.09	1	31308.6	(0) (1.04) 1.42? <b>2.50</b>	(0) (1.00) 1.50 <b>2.50</b>

	$p_1 \ 2^{1/2}$		$p_2 \ 1^{1/2}$		$p_3 \ 1^{1/2}$
$d_1 \ 3^{1/2}$	29952.4				
	<b>659.2</b>				
$d_2 \ 2^{1/2}$	30611.6	<b>1043.9</b>	29567.7		
	<b>697.0</b>		<b>696.7</b>		
$d_3 \ 1^{1/2}$	31308.6	<b>1044.2</b>	30264.4	<b>375.0</b>	29889.4

It is seen in these groups that the ratios of the term differences depart greatly from the interval rule of LANDÉ. They also give a good idea of the agreement between observed and calculated ZEEMAN effects.

It is remarkable that in his interesting paper on triplet combinations S. POPOW <sup>1)</sup> already suspected that the last group was a triplet *pd* combination.

In the calculation of the relative term-values the term  $p_1$  was put equal to 0; it is, however, uncertain whether this term represents the highest or the lowest of the levels of energy.

TABLE A. OTHER COMBINATIONS.

Combination	$\lambda$	I	$\nu_{vac.}$	ZEEMAN effect	
				observed	calculated
<b><math>\bar{p}_1</math> <math>2^{1/2}</math> with</b>					
I $2^{1/2}$	4296.21	8 <sub>r</sub>	23269.8 (0)	1.49	(0) 1.50
$\bar{d}_1$ $3^{1/2}$	4526.30	5	22086.9 (0)	1.11	(0) 1.00 1.17 1.33...
II $1^{1/2}$	4559.51	2	21926.0 (0)	1.67	(0) 1.72
III $1^{1/2}$	4716.59	(8)	21195.8 (0) (0.65)	0.86 1.45 2.13	(0) (0.63) 0.85 1.50 2.13
$\bar{d}_2$ $2^{1/2}$	4724.57	(5)	21160.0	—	—
IV $2^{1/2}$ ?	4952.21	(4)	20187.4 (0)	1.21	0.84 (1.32) 1.50
V $1^{1/2}$	5063.07	(2)	19745.4	—	—
VI $3^{1/2}$	5464.57	(5)	18294.6	—	—
VII $2^{1/2}$	5482.47	(6)	18255.0	—	—
<b><math>\bar{p}_2</math> <math>1^{1/2}</math> with</b>					
I $2^{1/2}$	4204.23	4 <sub>r</sub>	23778.9 (0)	1.48	(0) 1.50
II $1^{1/2}$	4455.99	2	22435.4 (0.20)	1.40	(0.22) 1.28 1.50
III $1^{1/2}$	4605.99	2	21704.8 (0.62)	0.85 1.51	(0.63) 0.87 1.50
$\bar{d}_3$ $2^{1/2}$	4613.57	4	21669.1	—	—
IV $2^{1/2}$ ?	4830.68	(2)	20695.2 (0)	0.76	(0) 0.18 (0.66) 0.84 1.50
V $1^{1/2}$	4935.77	(2)	20254.6	—	—
VII $2^{1/2}$	?				
<b><math>\bar{p}_3</math> <math>1^{1/2}</math> with</b>					
II $1^{1/2}$	4364.84	3	22903.9 (0)	1.27	(0) 1.28
III $1^{1/2}$	?				
V $1^{1/2}$	4824.22	(8)	20723.0 (0)	0.78	(0) 0.78

<sup>1)</sup> S. POPOW, Ann. der Phys. 45, 147, 1914.

The calculated resolutions of the terms treated above were the starting-point for the calculation of the other term resolutions of the combinations following. As these resolutions could be calculated from different combi-

TABLE A (continued).

Combination	$\lambda$	I	$\nu_{vac.}$	ZEEMAN effect	
				observed	calculated
<b>d<sub>1</sub> 3<sup>1/2</sup> with</b>					
I 2 <sup>1/2</sup>	3808.89	2	26246.9 (0)	1.20	(0) <b>1.00</b> 1.17 1.33...
$\bar{d}_1$ 3 <sup>1/2</sup>	3988.66	30	25064.0 (0)	1.32	(0) 1.33
$\bar{d}_2$ 2 <sup>1/2</sup>	4141.90	10	24142.6 (0)	1.49	(0) <b>1.67</b> 1.40
IV 2 <sup>1/2</sup>	4316.07	1	23162.7 (0) (0.55) (1.10)	1.98 <b>2.35</b>	(0) (0.50) (1.00) 1.55 <b>2.35</b>
VI 3 <sup>1/2</sup>	4699.80	(2)	21271.6	—	—
VII 2 <sup>1/2</sup>	4713.08	(8)	21211.6 (0) (0.47) (0.92)	1.83 <b>2.26</b>	(0) (0.45) (0.91) 1.79 <b>2.24</b>
<b>d<sub>2</sub> 2<sup>1/2</sup> with</b>					
I 2 <sup>1/2</sup>	3715.67	4	26905.3 (0.64) 0.81 <b>1.15 1.51 1.78?</b>	(0.67) 0.83 <b>1.16 1.50</b>	1.84
$\bar{d}_1$ 3 <sup>1/2</sup>	3886.51	15	25722.7 (0)	1.53	(0) <b>1.67</b> 1.40...
II 1 <sup>1/2</sup>	3910.95	(2)	25562.0 (0)	1.05	(0) 1.05
III 1 <sup>1/2</sup>	4026.03	4	24831.4 (0)	1.33	(0) <b>1.46</b> 1.16...
$\bar{d}_2$ 2 <sup>1/2</sup>	4031.86	7	24795.5 (0)	1.15	(0) 1.16
IV 2 <sup>1/2</sup>	4196.74	10	23821.3 (0.39) 0.52 (0.60) <b>0.81 1.14</b> [1.41]	(0.32) 0.52 (0.64) <b>0.84 1.16</b> [1.49]	
V 1 <sup>1/2</sup>	4275.80	4	23380.9 (0) (0.36) 1.13 <b>1.51</b>	(0) (0.38) 1.16 <b>1.55</b>	
VI 3 <sup>1/2</sup>	4558.66	4	21930.2 (0)	0.93	(0) <b>0.82</b> 0.94 1.05...
VII 2 <sup>1/2</sup>	4571.14	(2u)	<b>21870.4</b> (0.43)	1.00	(0.57) 0.88 <b>1.16</b>
<b>d<sub>3</sub> 1<sup>1/2</sup> with</b>					
I 2 <sup>1/2</sup>	3621.96	1	27601.4 (0) (1.06)	2.52	(0) (1.00) 2.50
II 1 <sup>1/2</sup>	?				
III 1 <sup>1/2</sup>	3916.21	10	25527.7 (0.38) <b>0.47</b> 0.89	(0.37) <b>0.50</b> 0.87	
$\bar{d}_2$ 2 <sup>1/2</sup>	3921.71	10	25491.9 (0) 0.57 (0.64) 1.19 <b>1.82</b>	(0) 0.50 (0.66) 1.16 1.87	
IV 2 <sup>1/2</sup>	4077.51	15	24517.9 (0) (0.37) 0.50 0.84 <b>1.18</b>	(0) (0.34) 0.50 0.84 <b>1.18</b>	
V 1 <sup>1/2</sup>	4152.17	10	24077.0 (0.29) 0.48 <b>0.78</b>	(0.28) 0.50 0.78	
VII 2 <sup>1/2</sup>	4430.11	8	22566.5 (0) (0.43)... 0.90? <b>1.34</b>	(0) (0.38) 0.50 0.90 <b>1.26</b>	

nations, the means of the  $g$  values found were given in the term table with the possible deviations. This was, of course, not necessary for the ordinary terms of the first rank of which the exact values of  $g$  have been given by LANDÉ.

Table A gives the other combinations between the terms given above with the observed and the calculated ZEE MAN effects. The latter have been calculated with the mean  $g$ -values given in the term-table.

TABLE A (continued).

Combination	$\lambda$	I	$\nu_{vac.}$	ZEE MAN effect	
				observed	calculated
<b>D <math>2^{1/2}</math> with</b>					
p <sub>1</sub> $2^{1/2}$	3142.99	1	31807.6	—	—
p <sub>2</sub> $1^{1/2}$	3249.33	3	30765.1	(0) <b>0.47</b> (0.49) 1.02	(0) <b>0.50</b> (0.50) 1.00
I $2^{1/2}$	3557.40	1	28102.4	—	—
$\bar{d}_1$ $3^{1/2}$	3713.71	6	26919.6	(0) (0.32) (0.64) 1.72 <b>2.06</b>	(0) (0.33) (0.67) 1.67 <b>2.00</b>
II $1^{1/2}$	3736.02	5	26758.9	—	—
III $1^{1/2}$	3840.92	5	26028.0	(0) 1.05	(0) <b>1.13</b> 1.00
$\bar{d}_2$ $2^{1/2}$	3846.16	3	25992.6	(0.28) 1.12	(0.33) 1.00 1.16
IV $2^{1/2}$	3995.91	5 <sub>r</sub>	25018.6	(0.27) 0.90	(0.32) 0.84 1.00
V $1^{1/2}$	4067.52	8	24578.1	(0) 1.09	(0) <b>1.22</b> 1.00
VI $3^{1/2}$	4322.69	5	23127.3	(0) 1.08	(0) <b>1.15</b> 1.10 1.05
VII $2^{1/2}$	4333.97	15	23067.0	(0.19) 0.95	(0.24) 0.88 1.00
<b>VIII <math>2^{1/2}</math> with</b>					
p <sub>1</sub> $2^{1/2}$	3010.92	(2)	33202.8	—	—
p <sub>2</sub> $1^{1/2}$	3108.57	(2)	32159.8	—	—
I $2^{1/2}$	?				
$\bar{d}_1$ $3^{1/2}$	3530.80	1	28274.1	—	—
II $1^{1/2}$	3550.98	1	28153.2	—	—
III $1^{1/2}$	3645.57	8	27422.7	(0) 0.63	(0) 0.59
$\bar{d}_2$ $2^{1/2}$	3650.31	4	27394.6	0.29 <b>0.73</b> (0.87) <b>1.17</b> 1.60	0.30 <b>0.73</b> (0.87) <b>1.16</b> 1.60
IV $2^{1/2}$	3784.95	2	26413.0	(0.17) 0.79	(0.22) 0.73 0.84
V $1^{1/2}$	3849.20	10	25972.1	(0) 0.69	(0) 0.68
VI $3^{1/2}$	4076.85	2	24521.8	(0) (0.35) (0.61) 1.33 <b>1.67</b>	(0) (0.32) (0.64) 1.37 <b>1.69</b>
VII $2^{1/2}$	4086.90	20	24461.5	(0.27) 0.81	(0.30) 0.73 0.88

TABLE B. LINES WITH KNOWN ZEEMAN EFFECT, WHICH HAVE NO PLACE AS YET IN THE TERM SYSTEM.

$\lambda$	I	$\nu_{vac}$	ZEEMAN effect observed	Combination $f_1 g_1$ with $f_2 g_2$	
3104.76	1	32199.3	(0) (0.50)... 1.49	$2\frac{1}{2}$ 1.00	$1\frac{1}{2}$ 0.50
3513.06	1	28457.1	0.54 (0.57) 1.08	$1\frac{1}{2}$ 0.54	$1\frac{1}{2}$ 1.08
3725.24	3	26836.3	(0) (0.39) (0.74) 1.47 1.82	$2\frac{1}{2}$ 0.73	$3\frac{1}{2}$ 1.10
4152.97	5	24072.4	0.32 <b>0.64</b> (0.76) <b>1.05</b> 1.42	$2\frac{1}{2}$ 0.66	$2\frac{1}{2}$ 1.05
4238.57	10	23586.2	(0.64) <b>0.73</b> <b>1.00</b> <b>1.30</b> 1.60	$2\frac{1}{2}$ <b>1.00</b>	$2\frac{1}{2}$ 1.30
4250.17	6	23521.8	(0.65) 0.66 <b>0.98</b> <b>1.30</b> 1.60	$2\frac{1}{2}$ 1.00	$2\frac{1}{2}$ 1.32
4300.59	3	23246.1	<b>0</b> <b>0.73</b> (0.73) <b>1.46</b> ( <b>1.50</b> ) 2.18	$2\frac{1}{2}$ 0.73	$2\frac{1}{2}$ 1.46
4383.62	5	22805.8	(0) (0.42) (0.87) 1.50 <b>1.89</b>	$2\frac{1}{2}$ 0.64	$3\frac{1}{2}$ 1.06
4436.02	1	22536.4	(0) (0.57) (1.19) 1.80 <b>2.43</b>	$2\frac{1}{2}$ 0.60	$3\frac{1}{2}$ 1.20
4474.72	(3)	22341.5	(0) (0.76) 1.11 <b>1.84</b>	$2\frac{1}{2}$ 1.10	$1\frac{1}{2}$ 0.36
4575.08	4	21851.4	(0.48) 0.51 <b>0.95</b> ( <b>0.98</b> ) <b>1.46</b> 2.07	$2\frac{1}{2}$ <b>0.98</b>	$2\frac{1}{2}$ 1.48
4647.64	1	21510.3	(0) (0.44) (0.86) 1.74 <b>2.15</b>	$2\frac{1}{2}$ 0.88	$3\frac{1}{2}$ 1.30
4669.10	3	21411.4	(0) (0.40) (0.72) 1.51 <b>1.86</b>	$2\frac{1}{2}$ 0.75	$3\frac{1}{2}$ 1.12
4728.55	(10)	21142.2	(0) (0.39) (1.59) 1.89	$2\frac{1}{2}$ 1.11	$1\frac{1}{2}$ 0.72
4804.22	(7)	20809.2	0.55 (0.93) 1.43	$1\frac{1}{2}$ 0.55	$1\frac{1}{2}$ 1.43
4946.60	(5)	20210.3	(0) (0.62) 1.17 1.81	$2\frac{1}{2}$ 1.17	$1\frac{1}{2}$ <b>0.54</b>
4986.99	(6)	20046.6	(0) (0.46) 0.95 <b>1.40</b>	$2\frac{1}{2}$ 0.95	$1\frac{1}{2}$ 0.50

TABLE C. CLASSIFIED LINES.

$\lambda$	I	$\nu_{vac}$	Combination	$\lambda$	I	$\nu_{vac}$	Combination
3010.92	(2)	33202.8	$p_1$ VIII	3513.06	1	28457.1	—
3104.76	1	32199.3	—	3530.80	1	28274.1	$\bar{d}_1$ VIII
3108.57	(2)	32159.8	$p_2$ VIII	3550.98	1	28153.2	II VIII
3142.99	1	31807.6	$p_1$ D	3557.40	1	28102.4	I D
3193.09	1	31308.6	$p_1$ $d_3$	3621.97	1	27601.4	I $d_3$
3249.49	3	30765.1	$p_2$ D	3637.35	3	27484.7	$p_1$ $\bar{p}_2$
3265.79	4	30611.6	$p_1$ $d_2$	3645.57	8	27422.7	III VIII
3303.26	5	30264.4	$p_2$ $d_3$	3650.31	4	27394.6	$\bar{d}_2$ VIII
3337.67	15	29952.4	$p_1$ $d_1$	3706.02	5	26975.5	$p_1$ $\bar{p}_1$
3344.71	7	29889.4	$p_3$ $d_2$	3713.71	6	26919.6	$\bar{d}_1$ D
3381.10	10	29567.7	$p_2$ $d_2$	3715.03	3	26910.0	$p_2$ $\bar{p}_3$

The wave-lengths and intensities are borrowed from the Handbuch of KAYSER according to EXNER and HASCHEK's observations, (spark

$\lambda$	I	$\nu_{vac.}$	Combination	$\lambda$	I	$\nu_{vac.}$	Combination
3715.67	4	26905.3	I $d_2$	4316.07	1	23152.7	IV $d_1$
3725.24	3	26836.3	—	4322.69	5	23127.3	VI D
3736.02	5	26758.9	II D	4333.97	15	23057.0	VII D
3780.85	3 <sub>r</sub>	26441.6	$p_2$ $\bar{p}_2$	4364.85	3	22903.9	II $\bar{p}_3$
3784.95	2	26413.0	IV VIII	4383.62	5	22805.8	—
3808.89	2	26246.9	I $d_1$	4430.11	8	22566.5	VII $d_3$
3835.29	5	26066.3	$p_3$ $\bar{p}_1$	4436.02	1	22536.4	—
3840.92	5	26028.0	III D	4455.99	2	22435.4	II $\bar{p}_2$
3846.16	3	25992.6	$\bar{d}_2$ D	4474.72	(3)	22341.5	—
3849.20	10	25972.1	V VIII	4526.30	5	22086.9	$\bar{d}_1$ $\bar{p}_1$
3855.10	3	25932.3	$p_2$ $\bar{p}_1$	4558.66	4	21930.2	VI $d_2$
3886.51	15	25722.7	$\bar{d}_1$ $d_2$	4559.51	2	21926.0	II $\bar{p}_1$
3910.95	(2)	25562.0	II $d_2$	4571.14	(2 <sub>n</sub> )	21870.4	VII $d_2$
3916.21	10	25527.7	III $d_3$	4575.08	4	21851.4	—
3921.71	10	25491.9	$\bar{d}_2$ $d_3$	4605.99	2	21704.8	III $\bar{p}_2$
3988.66	30	25064.0	$\bar{d}_1$ $d_1$	4613.57	4	21669.1	$\bar{d}_2$ $\bar{p}_2$
3995.91	5 <sub>r</sub>	25018.6	IV D	4647.64	1	21510.3	—
4026.03	4	24831.4	III $d_2$	4669.10	3	21411.4	—
4031.86	7	24795.5	$\bar{d}_2$ $d_2$	4699.80	(2)	21271.6	VI $d_1$
4067.52	8	24578.1	V D	4713.08	(8)	21211.6	VII $d_1$
4076.85	2	24521.8	VI VIII	4716.59	(8)	21195.8	III $\bar{p}_1$
4077.51	15	24517.9	IV $d_3$	4724.57	(5)	21160.0	$\bar{d}_2$ $\bar{p}_1$
4086.90	20	24461.5	VII VIII	4728.55	(10)	21142.2	—
4141.90	10	24142.6	$\bar{d}_2$ $d_1$	4804.22	(7)	20809.2	—
4152.17	10	24077.0	V $d_3$	4824.22	(8)	20723.0	V $\bar{p}_3$
4152.97	5	24072.4	—	4830.68	(2)	20695.2	IV $\bar{p}_2$ ?
4196.74	10	23821.3	IV $d_0$	4935.77	(2)	20254.6	V $\bar{p}_2$
4204.23	4 <sub>r</sub>	23778.9	I $\bar{p}_2$	4946.60	(5)	20210.3	—
4238.57	10	23586.2	—	4952.21	(4)	20187.4	IV $\bar{p}_1$ ?
4250.17	6	23521.8	—	4986.99	(6)	20046.6	—
4275.80	4	23380.9	V $d_2$	5063.07	(2)	19745.4	V $\bar{p}_1$
4296.21	8 <sub>r</sub>	23269.8	I $\bar{p}_1$	5464.57	(5)	18294.6	VI $\bar{p}_1$
4300.59	3	23246.1	—	5482.47	(6)	18255.0	VII $\bar{p}_1$

spectrum), those where the intensities are placed between brackets according to WOLFF, (arc-spectrum).

Table B gives the lines, for which the observed ZEEMAN effect renders a calculation of  $J$  and  $g$  for initial and final state possible, but which cannot yet be classed in the above-given term system. For some of these lines the result is uncertain, possibly because not yet all the parallel components have been observed.

Table C gives the classified lines.

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**Histology.** — “*The innervation of the muscle-fibres of the myo-cardium and of the atrioventricular bundle of HIS in the heart of the tortoise (emys and cyclemys).* (1st Communication). By Prof. J. BOEKE.

(Communicated at the meeting of November 29, 1924).

In no organ the innervation problem is of such a fundamental importance both for the physiology and for the pathology of it, as it is in the heart-muscle. In no organ, however, the histological study of the innervation meets with so many difficulties and obstacles as in the heart-muscle.

Although there is still some discussion going on about histological details, the mode of innervation of the cross-striated muscle-fibres, the form and distribution of the motor endplates on them, their connection with the muscle-fibres, are well known. In the heart-muscle it is not even known, whether there are distinct nerve-endings on the muscle-cells, or whether there is simply a plexus of nerve-fibres running between the muscle-fibres without distinct endings being formed. In his splendid and exhaustive treatise on the innervation of the heart<sup>1)</sup> published in 1908 MOLLARD draws the conclusion “qu'à l'heure actuelle on ne connaît pas encore d'une façon certaine et définitive le mode de terminaison des nerfs dans le myocarde. L'existence de terminaisons motrices établies sur le type de celles les plus simples des muscles striés ordinaires (RENAUT) n'est pas démontrée, non plus que l'existence d'un type spécial de terminaisons différent à la fois de celles des muscles striés qui sont enveloppées dans un sarcolemme, et de celles des muscles lisses (SMIRNOW)” (l. c. p. 185). And even to-day we have to confess that this statement is true.

It has been amply demonstrated for the different classes of the higher vertebrates, how extraordinarily rich in nerve fibres throughout its whole extent the myocardium is, but we are still quite ignorant about the way on which these nerve-fibres are connected with the contractile elements themselves. The majority of the investigators of the subject, and among them especially the authors, who have most thoroughly studied the innervation of the heart-muscle, lay much stress on the fact, that though it is possible to demonstrate a network of very fine nerve fibres surrounding the muscular elements on all sides, no trace of distinct free nerve-endings is to be found. The apparently free endings of the nerve fibres, which show themselves here and there in the preparations, must not be considered as real free nerve-endings, but as the results of a break in the impregnation of the nerve-fibres, a common feature of the

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<sup>1)</sup> J. MOLLARD. Les nerfs du coeur. Revue générale d'Histologie. Fascicule 9. 306 pages, 79 figures. 1908.

GOLGI-impregnation-method, consequently as a fault of the technique employed in the investigation, and not as a histological reality (HOFMANN). Even a pastmaster of the technique of the staining of the elements of the nervous system as DOGIEL only succeeded in demonstrating in the heartmuscle of the tortoise a very fine network of delicate nerve fibres surrounding the muscle cells, and finished his description of the mode of innervation by saying that in one of his preparations in one and only one place he had got the impression, that there were small knob-like nerve-endings to be seen <sup>1)</sup>, attached to the surface of the muscle-fibres. The drawing which has to illustrate this point is however not convincing. MICHAÏLOW <sup>2)</sup> who in the year 1909 applied the impregnation-method of CAJAL to the heart muscle of the frog, described (just as JACQUES in 1902) distinct ramified nerve-endings on the muscle-cells of the heart, which he took for the endings of the vagus nerve; in addition to these endings he found again the same delicate varicose nerve-plexus surrounding the heart muscle-cells as described by former investigators. According to him however the existence of distinct end-branches, ending in a neurofibrillar ending or endloop on the surface of the muscular elements is undeniable. These endings never enter the muscle-cells themselves. The earlier statements by RANVIER "que les fibrilles nerveuses pénètrent réellement dans les cellules musculaires et qu'elles passent au voisinage de leur noyaux" (1878, 1880) were the results of a defective technique and in consequence an incorrect observation.

Recent investigations have not been able to alter these views. The standpoint of the majority of the investigators to-day is essentially the same as was that of MICHAÏLOW and DOGIEL in the year 1907 and of GORDON WILSON in the year 1909. Extensive researches, it is true, on the minor details of the innervation of the cardiac muscle-elements, these later years did not bring us. The authors confirmed themselves to the investigation of the distribution of the ganglion cells in the wall of the heart, their connections with the cardiac nerves, their number in the different parts of the heart in different animals, and to the distribution and form of the sensory nerve-endings in the endocard and in the pericard.

This is not to be wondered at, for I don't know of any other tissue, which refuses so obstinately to take a nerve-stain as does the cardiac muscle. For years I have tried again and again to stain the nerve-fibres of the heart-muscle and their endings with the same method, which gave excellent results in the skeletal muscles of the self-same animals, but without success. It was only this year that by means of the neurofibrillar staining-method of BIELSCHOWSKY with a somewhat modified length of

<sup>1)</sup> J. DOGIEL. Einige Daten der Anatomie des Frosch- und Schildkrötenherzens. Arch. f. mikrosk. Anatomie. 70. Bd. 1907.

<sup>2)</sup> S. MICHAÏLOW. Internat. Monatschrift f. Anat. u. Physiologie. 25. Bd. 1909.

impregnation-time in the Ag NO<sub>3</sub>-solution (6 to 6½ days at a temperature of 35° C) I succeeded in getting good preparations with an excellent and elective colouring of the nerve-fibres and their endings in the cardiac muscle of the heart of tortoises and birds, and with tolerable results in the heart of the hedgehog.

In this communication however I will confine myself to the description of the distribution of the nerve-fibres and of the relations between the nerve-fibres and their terminal ramifications and the muscular elements, and the innervation of the muscular elements of the atrioventricular connection (bundle of His), in the heart of the tortoises (*emys europaea*, the European Pond-tortoise, and *cyclemys* sp.), because with those hearts I obtained the best and most complete results.

The form and arrangement of the elements of the cardiac muscle in the chelonian heart, their curious elongated and branched appearance, with the rod-shaped or oval nucleus in the middle, lying in a large quantity of granular sarcoplasm and surrounded by a ring of myofibrillae, which are freely continuous and pass over without interruption from one cell into the adjacent cells, is essentially the same in the heart of the lizard and in that of the cheloniae, and has been described by a number of authors. The arrangement of the muscular fibres, running in bundles, which are closely interwoven in the ventricular portion of the heart, but form a spacious network with thin strands of tissue and wide meshes in the auricular portion, may be considered also as sufficiently known after the descriptions given by BOTAZZI, DOGIEL, KÜLBES and LANGE, LAURENS and ENELLI. This arrangement too has essentially the same features as in the lizard heart, as it was described recently by KRAUSE (1923), and so there is no need to describe these things again here in full.

In preparations stained after the pyridine-silver method of BIELSCHOWSKY, treated afterwards with chloride of gold, and stained lightly with haematoxylin and eosin, the cardiac muscle-fibres show a very delicate but distinct cross-striation of the myofibrillae, and appear to be surrounded by a thin sarcolemma which is connected with the myofibrillae by very delicate but distinct cross-membranes of KRAUSE. The muscle cells are united by their branches into a syncytium without a trace of cellboundaries or junctional lines.

In the wall of the ventricle, as was stated before, the muscle-fibres are arranged in thick bundles, closely interwoven, and running in the sections apparently in all directions without any attempt at regularity. A closer study of serial sections however reveals a distinct regularity of arrangement. I may refer here to the excellent description given by BOTAZZI <sup>1)</sup>.

The wall of the ventricle is not a compact structure. Everywhere it

<sup>1)</sup> F. BOTAZZI. Ricerche sulla muscolatura cardiaca dell' *Emys europaea*. Zeitschr. . Allgem. Physiologie VI. 1907, p. 140—194.

consists of a network of closely interwoven bundles of muscle fibres, covered by the endocardium. These bundles however do not form generally a regular cavernous or sponge-like tissue, but they enclose a more or less spacious central cavity, which by means of the ostium atrioventriculare is connected with the cavity of both auricles, and surrounding it a system of additional cavities, so that the blood flows freely between all the bundles of muscle fibres and these bundles even quite near the outer epicardium-covered surface of the ventricular wall are lined by the endocardium.

In the auricles the system of trabeculae is much more spacious, so that the entire auricular wall is much thinner and the bundles are composed of a smaller number of muscle fibres and are lying more widely apart. Here too all the trabeculae are everywhere lined by endocardium, and in the sections the thinner bundles of muscle fibres are often seen to be connected here by thin bands, consisting only of endocardium without a trace of muscle fibres enclosed by it.

In the septum atriorum, the sinus venosus and the wall of the central ventricular cavity we find underneath the endothelial lining of the endocardium in thick bundles the curious layer of smooth muscle cells, described by GASKELL, ROSENZWEIG, BOTAZZI, which abuts on the tunica media of the large veins of the heart (c.f. LAURENS 1913) and which ROSENZWEIG, BOTAZZI and OINUMA held responsible for the oscillations of the tonus of the tortoise heart. LAURENS could find them only in the wall of the auricles, but without doubt they occur also in the wall of the ventricle. BOTAZZI compares them with the fibres of PURKINJE of the mammalian and avian heart.

Now in the first place we find even in the mammalian heart in the connective tissue underlying the endocardium-endothelium in places scattered bundles of non-striped muscle, as first pointed out by SCHWEIGGER-SEIDEL, which have nothing to do with the fibres of PURKINJE and the bundle of HIS-TAWARA. And secondly we find in the septum atriorum and the dorsal wall of the atria bundles of curious branched *cross-striated* muscle-cells (fig. 6), lying as a loose network in the connective tissue, which may be traced in the sections as an uninterrupted bundle into the wall of the ventricle, which with a better right may be compared with the bundle of HIS and the fibres of PURKINJE. But about this point we have more to say later on.

The innervation and the intracardial nervous system of the tortoise (and in general reptilian) heart has been described by a number of authors. For the description of the distribution of the nerves and their course in the heart wall as far as it is visible to the naked eye I can refer the reader to the paper by DOGIEL and ARCHANGELSKY<sup>1)</sup> and to

<sup>1)</sup> Pflüger's Arch. f. d. Ges. Physiologie 113. Bd. U. 1.  
J. DOGIEL. Arch. f. mikrosk. Anatomie 70. Bd.

the paper by LAURENS<sup>1)</sup>). Nerves can be seen running along the superior venae cavae to the heart. On the right side a branch, the coronary nerve, runs directly from the sinus under the vein to the ventricle, the remainder of this nerve being distributed to the sinus and perhaps a small branch to the right auricle (LAURENS). The nerve on the right side is distributed principally to the left auricle from which can be made out several branches which run to the ventricle along the auriculo-ventricular groove, some ending here and others continuing on to the dorsal surface of the ventricle. Running to the ventral side of the heart are several fine branches which divide and are distributed to the different vessels of the bulbus aortae. The dorsal ligamentum atrioventriculare of DOGIEL contains one or more large nerve branches running to the ventricle, and numerous ganglion cells. According to LAURENS, whose description I follow here, groups of ganglion cells are more numerous in the tortoise heart than in that of the lizard. The largest are two at the opening of the sinus and of the pulmonary veins into the auricles. As was mentioned already, in the dorsal ligament there are numerous groups of ganglia all along the course of the coronary nerve. On the dorsal side of the left auricle, just under the pericardium, there are numerous small groups of ganglia to be seen, some consisting of only two or three cells. The same holds true for the wall of the ventricle. Here too there are a number of small subpericardial groups of ganglia, near the apex as well as near the coronary groove. At the beginning of the septum atriorum, on the right side, there is a collection of ganglia and also several small groups of nerve cells along this side of the septum. In the connective tissue of the auriculo-ventricular groove, particularly on the left side and in the proximity of the bulbus, the ganglionic masses are very numerous, though small, consisting of from two to five cells (LAURENS). In BIELSCHOWSKY-preparations the plexus around the ganglion cells appears to be very rich. By that reason it is impossible to trace distinct nerve-fibres to separate ganglion cells, or from them to the separate muscle fibres. Experimental work (cutting of the vagus and sympathetic nerve, etc.) may perhaps throw some light on this question too.

For the question of the finer details of the innervation the distribution and the course of the nerve-fibres as seen in the sections under the microscope is of more importance.

As it was described already years ago by GERLACH, the nerve-fibres of the heartwall form everywhere a network, a plexus. Large nerves do not enter into the heart-muscle, except the larger nerve-branches, described above, which originate from the groups of ganglia in the septum atriorum and the neighbourhood of the large veins of the heart and pass from here to the wall of the auricles and of the ventricle.

The ramifications of these nerves form a dense nerve-plexus under the endocardium (the "groundplexus" of GERLACH and HOFFMANN).

<sup>1)</sup> Anat. Record. Vol. VII.

This groundplexus is very rich, and consists of coarser nerve-strands in the wall of the ventricle, and of very fine nerve-threads in the trabeculae of the auricles. From this fundamental sub-endocardial plexus arise numerous fine fibres, which terminate at different levels of the endocardium in more or less complicated sensory nerve-endings. The heart is, just as in the higher vertebrates, supplied as abundantly with afferent nerves as is the most sensitive skinsurface.

But in this groundplexus are running also the efferent nerve-fibres, and indeed, when we study the plexus there where it lies under the endocardium of the trabeculae carneae of the auricles, or of the finer muscle-bundles of the ventricular wall, we get the impression that this nerveplexus, whose branches, consisting of very fine nerve-threads, are seen running in different directions even on the smallest trabecles of the atria, is chiefly of an efferent nature, as will be discussed below.

There is no part of the muscle-bundles to be found, where this subendocardial nerve-plexus is absent. We find it even on the smallest muscle-columns of the auricles and of the ventricle, and even there, where as was described before, two of the trabeculae carneae of the auricles are connected by a strand, consisting only of endocardial tissue, without a single muscle-fibre in it, we often see a very delicate neurofibrillar strand running inside this endocardial thread and connecting the groundplexus of one trabecle with that of the other.

Whether the branches of this nerve-plexus form closed meshes or not, is difficult to state. Everywhere we see the neurofibrillar strands branching and ramifying on the surface of the muscle-columns, but where in the sections in most cases only fragments of the plexus are to be seen, it is difficult to state, whether branches of the neurofibrillar strands, once parted, come together again to unite into one single branch, or simply run across each other in different directions.

In a general way the drawing of the groundplexus around the trabecles of the auricle of the frogs heart, given by HOFMANN<sup>1)</sup>, furnishes also a good picture of the features of this plexus in the heart of the tortoise.

From this fundamental subendocardial plexus we see everywhere fine neurofibrillar strands passing into the muscle-columns. They are running here at first between the muscle-cells, as it is to be concluded from the study of cross-sections of the muscle-columns and from the fact, that in longitudinal sections of a muscle-bundle these nerve-fibres are often seen running at right angles to the long axis of the muscle-fibres, winding their way across two or three muscle-fibres. But when we follow these neurofibrillar strands during their course, we see them curve round very soon

<sup>1)</sup> F. B. HOFMANN. Das intracardiale Nervensystem des Frosches. Arch. f. Anat. und Physiol. Anat. Abtheilung 1902. Tafel IV.

F. B. HOFMANN. Histologische Untersuchungen über die Innervation der glatten und ihr verwandten Muskulatur der Wirbeltiere und Mollusken. Arch. f. mikrosk. Anatomie, 70, Bd. 1907.

and run on in the direction of the muscle-fibres. These nerve-fibres which are running parallel to the long axis of the muscular elements are nearly without exception varicose, the varicosities often following each other so regularly in the course of the nerve-fibre as to suggest the comparison with a string of beads.

Everywhere we see these delicate varicose threads running through the muscle-bundles, and in the straight long muscle-bundles we often meet in the sections through the wall of the ventricle, they are often to be followed a long way passing a number of muscle-nuclei. In the groups of muscle-fibres fixed in a contracted state they often appear as meander-like winded threads. Especially in the sections through the wall of the auricles the short thin muscle-columns running freely through the atrial cavity and often being composed of only two or three muscle-fibres, present even in thin sections (15—25  $\mu$ ) a very clear picture of the groundplexus underneath the endothelial lining and of the nerve-ramifications between the muscle-fibres inside.

Whether these different intermuscular branches are still running exclusively between the muscle-fibres or are lying already imbedded in the protoplasm of the fibres themselves is not easily to determine in each case given. But it is certain, that *from these intermuscular nerve-threads branch off very fine varicose nerve-fibres, which pass into the muscle-cells and lie imbedded in the protoplasm itself.* They are extremely delicate, beset with small *irregular* varicosities, and either may be followed through two or even three muscle-cell territories, or end abruptly within the sarcoplasm with a small endnet or endloop or a series of terminal varicosities appearing as very small ring-like expansions of the neurofibrillar structure. In fig. 1 several of these nerve-endings are drawn from a section through the auricles, in fig. 2 a cross-section through part of a muscle-column of the ventricle shows the outline of some of the muscle-fibres, the one in the middle showing the nucleus and lying close to it imbedded in the sarcoplasm a small neurofibrillar ring at the end of an extremely delicate neurofibrille coming from the outer part of the muscle-fibre.

The clearness and distinctness of the impregnation of the neurofibrillae enabled us to ascertain with the utmost surety, that we had before us real endings of the neurofibrillar structure and not varicosities cut off by the microtome-knife. And indeed, we find those endings everywhere in the preparations, and where they are lying in the middle part of the sections, so that they are covered above and below by a layer of tissue, we may quite easily ascertain, whether they are real endings with rounded endloops or simply a place, where the neurofibrillar strand was cut across. Especially in the thin muscle-bundles of the auricles the intraprotoplasmic neurofibrillae with their varicosities and small endnets or endings were distinctly visible as such. In many cases the intraprotoplasmatic position of these neurofibrillar endings is made clear by their lying in exactly the same niveau as the nucleus in the clear nearly

uncoloured protoplasm, which surrounds the nucleus especially at both poles and which is surrounded by a ring of cross-striated myofibrillae. Inside this ring we often find the endloops of the neurofibrillar strands. This appears evident in those cases, as are drawn as exactly as possible in figg. 2, 4 and 5, where the neurofibrillar endring is lying quite close to the nucleus, sometimes even enclosing the top of the elongated nucleus. In this regard fig. 5 seems important; here a reticulated varicosity of the neurofibrillar strand was lying so close to the nucleus of a muscle-fibre, that it is making an indentation in the nucleus, and thus was lying in a cavity so deep, that at first sight it made the impression as if two nuclei were present, the neurofibrille passing between them. Only by focussing very carefully it became clear, that there was only one nucleus present, and that the neurofibrillar ring was lying close against it. Another endring too is shown in the same figure, lying also close against the side of the same nucleus. In cross-sections through the muscle-columns we see that the nerve-fibres, which run in the direction of the long axis of the muscle-fibres, are lying as a rule in the peripheral layer of the sarcoplasm, and one is tempted to ask, whether the principal intramuscular fibres, which were described as running with many curves apparently between the muscle-fibres, are in reality all of them lying between the muscle-fibres, and whether they are not, at least a number of them, already enclosed in the protoplasm of the muscle-fibres themselves.

The delicate varicose neurofibrillar threads furnished with endrings and endloops, whose intraprotoplasmic position could be made out convincingly, showed here and there a distinct connection with the sarcoplasm, an extremely delicate network, at one side continuous with the neurofibrillar structure, at the other side apparently passing into the cross-striation of the myofibrillae, at least with meshes, which in size correspond with the width of the cross-striation. In conformity with what is known about the motor-endplates on the cross-striated muscle-fibres of the voluntary muscles and their protoplasmic connection with the myofibrillae, it would be possible to identify this network with the *periterminal network* of the striped muscle-fibres.

In short, we find everywhere in the cardiac muscle an innervation of the individual contractile elements, consisting not only in a pericellular network, which encloses the muscle-fibre without definite nerve-endings (HOFMANN), but in a form, which on one hand reminds us of the mode of innervation of the non-striped muscle-fibres, as it was described for example in the musculus ciliaris of the human eye<sup>1)</sup>, on the other hand exhibits some features which remind us of the structure of the motor endplates on the striped muscle-fibre.

And finally, our observations seem to confirm to a certain degree the old statement by RANVIER, which was cited in the beginning of this

<sup>1)</sup> J. BOEKE. These Proceedings 17. p. 1982 and 18, p. 2.

paper, "que les fibrilles nerveuses pénètrent réellement dans les cellules musculaires et qu'elles passent au voisinage de leurs noyaux".

*Auriculo-ventricular bundle* (bundle of HIS). According to DOGIEL and ARCHANGELSKY (for the tortoise) and IMSCHANITZKY (for the lizard) the different parts of the reptile heart are not connected muscularly, the connection between the auricles and ventricle being effected solely by means of a large nerve bundle which runs in a band of connective tissue on the dorsal side of the heart, the "ligamentum atrioventriculare" of DOGIEL (1906).

It seems however, that the contradictory statement by a number of authors (f. ex. BOTAZZI, ROSENZWEIG, KÜLBS and LANGE, LAURENS) is convincing, and the existence of a funnel-shaped muscular connection between the auricular wall and the ventricle seems to be demonstrated beyond doubt.

But, as I mentioned before, it seems to me that two phenomena, which have nothing to do with each other, are often mixed up together in this respect. By BOTAZZI, in his paper cited on a previous page, much importance for the co-ordination of the heart is ascribed to the subendo-cardial layer of smooth muscle-cells described by him and by ROSENZWEIG and which forms a continuation of the tunica media of the large veins of the heart into the auricles and the ventricle <sup>1)</sup>, and when I understood rightly the short description, insufficiently illustrated, of KÜLBS and LANGE, these authors have the same elements in view, when they describe the voluminous funnelshaped muscular connection between the auricles and the ventricle. Now, as is pointed out by LAURENS, there exists without doubt a smaller funnelshaped connection between the auricles and the ventricle, consisting of *cross-striated muscle-fibres*, with a distinct but fine striation and large round or slightly oval nuclei, and of a brighter appearance than the ventricular fibres. This is the real bundle of HIS. It is thickest at the dorsal side of the auricles in the hind part of the septum atriorum, where we find the ligamentum atrioventriculare of DOGIEL, which forms a pathway for nerves and blood vessels and groups of ganglion cells between the sinus and the ventricle. This muscular connection, the real bundle of HIS, is composed of cross-striated muscle cells (c. f. LAURENS), which are more loosely arranged in the connective tissue than the muscular elements of both auricles and ventricle, and therefore present a more branched and netlike appearance (fig. 6), herein exhibiting the same features, which are so characteristic for the fibres of PURKINJE in the avian and mammalian heart. At one side this muscular bundle is connected with the auricular musculature, at the other side with the inner wall of the ventricle.

The striated muscular elements of this bundle receive an individual

<sup>1)</sup> According to LAURENS they occur only in the auricles, but they are distinctly visible also in the wall of the ventricle enclosing the central ventricular cavity.

**J. BOEKE: "The innervation of the muscle-fibres of the myocardium and of the atrioventricular bundle of His in the heart of the tortoise (emys and cyclemys").**

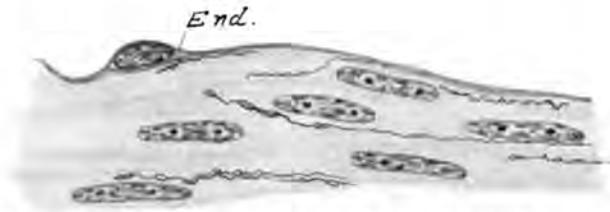


Fig. 1. Nerve-endings in a longitudinal section through a muscle-trabecle of the auricle of the heart of *emys europaea*.  
End. = Endocardium.

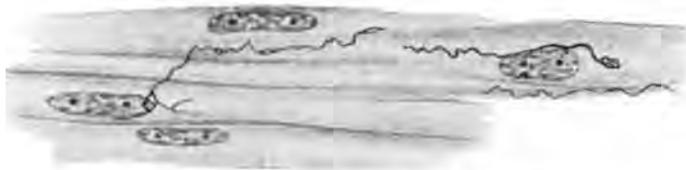


Fig. 2. The same from the wall of the ventricle.



Fig. 3. From a cross section through a muscle-column of the auricle, showing the nucleus of one of the fibres, and besides it an intraprotoplasmic neurofibrillar ending (foreshortened).

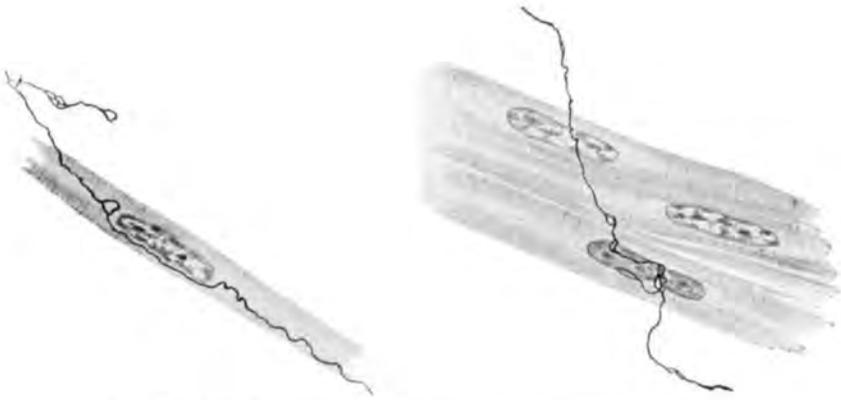


Fig. 4 and 5. Heartmuscle-fibres from the wall of the auricle of the tortoise heart with neurofibrillar nets lying close to the nucleus.



Fig. 6. Longitudinal section through the connective tissue of the septum coronarium with loosely connected muscle-fibres of the atrioventricular bundle of HIS, and on these fibres small terminal nerve-fibres (*nf.*).

efferent innervation in the same way as it was described in the foregoing pages for the muscle-cells of the auricles and the ventricle. Not only we find, running along it, the large nerve-bundle described above, and in connection with this numerous groups of ganglion cells, but the muscle-elements themselves possess an individual innervation (fig. 6), intraprotoplasmic nerve-fibres with neuro-fibrillar endings and varicosities (fig. 6nf), and a perimuscular nerve-plexus, which is certainly not less developed than around and in the muscle-columns of the auricles and the ventricle. Every individual muscle-fibre of the bundle of HIS is innervated.

In conclusion we may remark, that also in the subendocardial layer of smooth muscle-cells of BOTAZZI and ROSENZWEIG referred to above, a plexus of very delicate nerve-fibres with varicosities and small endnets could be traced throughout the whole layer. The strands of this plexus appeared to be in connection with the perimuscular nerve-plexus of the muscle-bundles lying underneath and seemed in many cases to be the direct continuation of this plexus.

*Utrecht, November 1924.*

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**Chemistry.** — “Equilibria in systems, in which phases, separated by a semi-permeable membrane”. III. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of November 29, 1924).

*Ternary systems with solid phases.*

We shall consider the membrane-diffusion-pressure and the osmotic attraction in ternary systems, in which one or more solid phases occur. For this reason we take at constant  $T$  and  $P$  the ternary systems  $W-X-Y$  in which  $W$  is the diffusing substance; in order to simplify the discussions, we shall assume that  $W$  is water; yet the deductions remain valid generally. For the sake of abbreviation we shall represent the membrane-diffusion-pressure of the water by  $M.D.P.W.$  and the osmotic water-attraction by  $O.W.A.$

1.  $M.D.P.W.$  and  $O.W.A.$  when one of the components  $X$  or  $Y$  occurs as solid phase.

In the figs 1—3 the saturation-curve of the component  $Y$  is represented by curve  $wv$ ; according to a known property, each straight line going through point  $Y$  is allowed to intersect this curve in one point only. We shall call  $w$  the hydrous and  $v$  the anhydrous terminating-point of this curve. Proceeding along this curve starting from  $w$  towards  $v$ , we arrive firstly in  $a$ , then in  $b$  etc.; we shall say that  $a$  is situated closer to  $w$  than  $b$ ,  $b$  closer to  $w$  than  $c$ , etc.

Going from  $w$  to  $v$ , we arrive, therefore, always further away from the hydrous terminating-point  $w$ , but hence the conclusion may not yet be drawn that the percentage of water of a liquid decreases always, the more it is situated further from  $w$ . This is really the case in the figs 1 and 3, in which all lines, parallel to the side  $XY$  intersect curve  $wv$  in one point only. In fig. 2 this is not the case, we imagine in this figure  $wc$  and the tangent in  $b$  parallel to  $XY$ . Starting from  $w$  the percentage of water of the liquid then firstly increases till in  $b$ , where it is a maximum; starting from  $b$  it decreases; in  $c$  the percentage of water is equal again to that in  $w$ .

We now shall deduce:

the more a liquid is situated further from the hydrous terminating-point of a saturation-curve, the greater the  $O.W.A.$  of a liquid of this saturation-curve is.

The osmotic attraction of water must, therefore, increase along curve  $wv$  in the direction of the little arrows on this curve. In figs 1 and 3 the  $O.W.A.$  of liquid  $a$  is, therefore, larger than that of  $w$ , that of  $b$

larger than that of  $a$ , etc.; consequently the *O.W.A.* increases, the more the percentage of water of the liquids becomes smaller. Otherwise it is, however, on part  $wc$  of curve  $wv$  in fig. 2. Although  $w$  and  $c$  have the same percentage of water, the *O.W.A.* of liquid  $c$  is larger than that of  $w$  and although  $b$  has a greater percentage of water than  $a$  or  $w$ , the *O.W.A.* of liquid  $b$  is greater than that of  $a$  and  $w$ .

We may deduce in different ways the property mentioned above.

It is clear that the *O.W.A.* of a saturated liquid  $a$  or  $b$  is defined by the isotonic curve of the water, which passes through the point  $a$  or  $b$ . Consequently we have to show that the point of intersection of curve  $wv$  with an isotonic curve is situated further away from the point  $w$ , the greater the *O.W.A.* of that isotonic curve is.

In figs 1—3 the isotonic curves are represented by dotted curves. As the *O.W.A.* of the liquids of those curves increases the more those curves are situated further away from the point  $W$ , the little arrows on the sides  $WX$  and  $WY$  indicate, therefore, the direction of increasing *O.W.A.* As we have formerly shown, those curves cannot intersect one another. Firstly we shall show:

an isotonic curve and the saturation-curve of a component can intersect one another in one point only, they never can touch one another.

In ternary systems viz. is valid the rule: two saturation-curves, each of a component, can intersect one another in one point only, they never can touch one another. When we now consider the isotonic  $W$ -curve like the saturation-curve of the component  $W$  in a definite imaginary state ( $W_1$ ), then at once the above-mentioned property follows from this.

This may be deduced in the following way also. We imagine above triangle  $WXY$  of figs 1—3 the  $\zeta$  surface  $W'X'Y'$  belonging to the assumed  $T$  and  $P$ . On the axis  $YY'$  we take a point  $Y''$  in such a way that  $YY''$  represents the  $\zeta$  of the solid component  $Y$ ; on the axis  $WW'$  we take a point  $W''$  in such a way that  $WW'' = \zeta(w_1)$ . The projection of the tangent-curve of a cone, touching the  $\zeta$  surface and having the top in  $Y''$ , is then the saturation-curve  $wv$ . The isotonic  $W$ -curve, the *O.W.A.* of which is defined by  $WW''$ , is the projection of the tangent-curve of a cone, touching the  $\zeta$  surface and having the top in  $W''$ .

The point of intersection of those two curves is defined, therefore, by the point of contact of the  $\zeta$ -surface with a tangent-plane, which passes through the line  $W''Y''$ . It is evident now that, when the  $\zeta$ -surface is downward convex in each point, there may be one similar tangent-plane only, consequently also one point of intersection only.

We now take an isotonic  $W$ -curve of such low *O.W.A.* that it doesn't intersect the saturation-curve  $wv$ ; on increase of the *O.W.A.* it moves away from the point  $W$  till in the stand  $wm$  it meets for the first time curve  $wv$ . Of all liquids of curve  $wv$ ,  $w$  has, therefore, the lowest *O.W.A.*

We now take the two liquids *a* and *b*. As those liquids, like we have deduced above, cannot be situated on a same isotonic curve, they are situated, therefore, on the two different curves *an* and *bo*, and as those curves can not intersect one another, they are situated with respect to another as is drawn in figs 1—3. Consequently the *O.W.A.* in *b* is greater than that in *a*. We find, therefore, the above-mentioned property:

the *O.W.A.* of a liquid of a saturation-curve is greater, the further this liquid is situated from the hydrous terminating-point of the curve.

Of course the reserve is the case with the *M.D.P.W.*

We may deduce this property also in the following way. The saturation-curve *wv* of the component *Y* is defined by:

$$\zeta - x \frac{\partial \zeta}{\partial x} + (1-y) \frac{\partial \zeta}{\partial y} = \zeta_y \dots \dots \dots (1)$$

in which  $\zeta_y$  represents the  $\zeta$  of the solid component *Y*. The *O.W.A.* and the *M.D.P.W.* depend on

$$\varphi = \zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \dots \dots \dots (2)$$

The *O.W.A.* increases at decreasing value of  $\varphi$ . From (1) and (2) follows at constant *T* and *P*:

$$[-xr + (1-y)s] dx + [-xs + (1-y)t] dy = 0 \dots \dots (3)$$

$$d\varphi = -(xr + ys) dx - (xs + yt) dy;$$

with the aid of (3) the latter equation passes into:

$$d\varphi = -s dx - t dy \dots \dots \dots (4)$$

We now may show that in no point whatever of curve *wv* *dφ* can become zero. In accordance with (4) should be necessary for this

$$s dx + t dy = 0 \dots \dots \dots (5)$$

while *dx* and *dy* satisfy (3) also. This can only be the case, when

$$rt - s^2 = 0 \dots \dots \dots (6)$$

consequently when the liquid under consideration is situated on the spinodal line of a region of dimixtion; we shall refer to this at the discussion of the dimixtion.

The *O.W.A.* changes, therefore, starting from *w* towards *v* always in the same direction, without showing a maximum or minimum. When we know in one point only of curve *wv* the direction, in which the *O.W.A.* increases or decreases, then, therefore, this direction is known for the whole curve also. For this reason we choose a point in the vicinity of point *w*. Then *x* becomes infinitely small in (3) and (4), while *xr* approaches *RT*. We now find:

$$d\varphi = -\frac{RT}{1-y} \cdot dx \dots \dots \dots (7)$$

so that  $d\eta$  is negative in the vicinity of the point  $w$ . Consequently  $\eta$  decreases, starting from  $w$ , so that the O.W.A. increases along curve  $wv$  starting from  $w$ .

We shall consider now the saturation-curve and an isotonic curve in the vicinity of their point of intersection, f.i. curves  $wv$  and  $nn'$  with

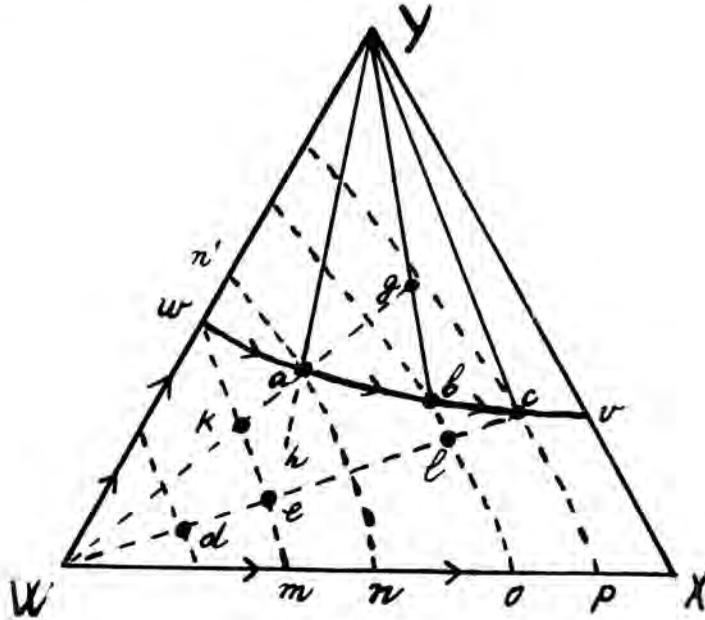


Fig. 1.

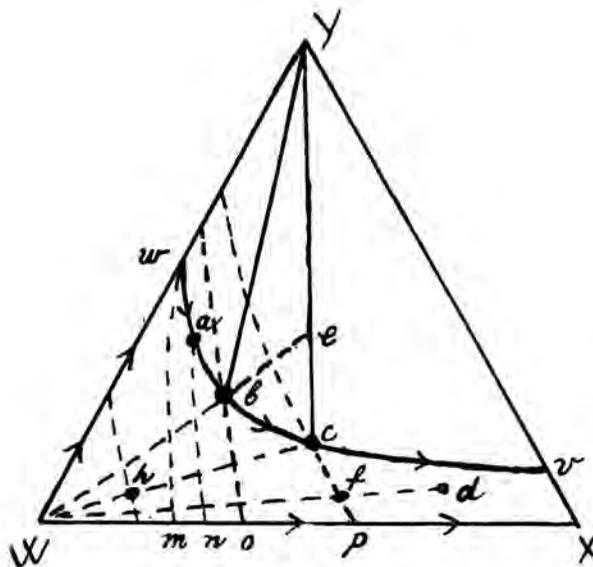


Fig. 2.

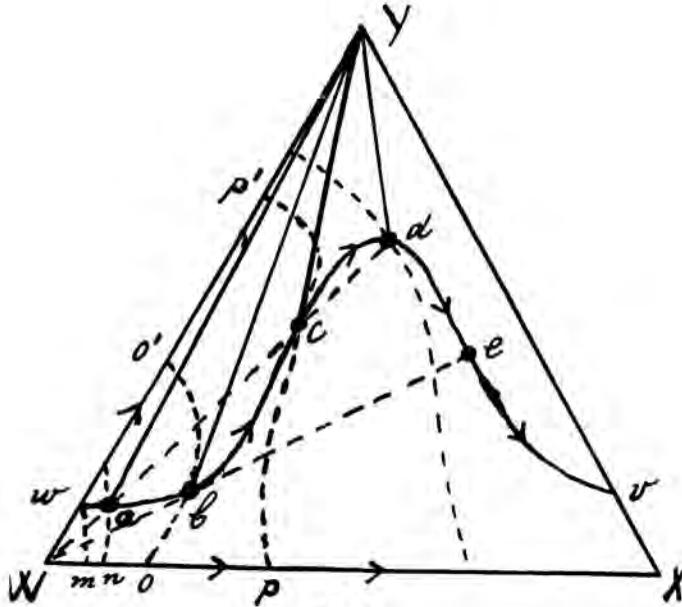


Fig. 3.

their point of intersection  $a$  in fig. 1. We shall call the angle  $WaY$  and its opposite angle  $hag$  the conjugation-angle of both curves, the angles  $Wah$  and  $Yag$  the supplement-angle.

Formerly<sup>1)</sup> we have deduced some rules for the intersection of two saturation-curves; when we replace in those rules one of the saturation-curves by an isotonic curve, then they become:

a saturation-curve and an isotonic curve are situated in the vicinity of their point of intersection either both within the conjugation-angle or both within the supplement-angle.

when the saturation-curve touches one of the sides of that angle, then the isotonic curve touches the other side.

If we imagine in the points  $a$ ,  $b$  and  $c$  of figs. 1 and 2 the conjugation angle to be drawn, then we see that in each of those points the saturation-curve is situated within the conjugation-angle, consequently the isotonic curve must also be situated within that angle; the same is the case in the points  $a$  and  $d$  of fig. 3. In point  $c$  of this figure the saturation-curve is situated within the supplement-angle, consequently the isotonic curve  $pcp'$  must also be situated within that angle. In point  $b$  of fig. 3 the saturation-curve touches the side  $Wbe$ ; the isotonic curve  $obo'$  must, therefore, touch  $bY$  in  $b$ .

When  $L_a$  viz. the saturated liquid  $a$  (figs 1–3) takes water, then it proceeds along the line  $aW$  starting from  $a$  in the direction towards

<sup>1)</sup> F. A. H. SCHREINEMAKERS. Die heterogenen Gleichgewichte von H. W. BAKHUIS ROOZEBOOM III' 73, 268.

In-, mono-, and plurivariant equilibria XXV (These Proceedings 27, p. 57).

$W$ ; it gets unsaturated and its  $O.W.A.$  becomes smaller. The same is true for all saturated solutions in figs 1 and 2.

When  $L_c$  (fig. 3) takes water, then the liquid proceeds, firstly with separation and afterwards again with solution of solid  $Y$ , along curve  $c b a$  and afterwards along the line  $a W$ . Also with this it appears again that on addition of water the  $O.W.A.$  becomes smaller.

When water is removed from  $L_a$  (fig. 1), so that the complex comes in  $g$ , then the liquid proceeds along curve  $a b$ ; consequently its  $O.W.A.$  increases.

Generally we may say:

at removing (addition) of water from (to) a liquid, its  $O.W.A.$  becomes greater (smaller), independent on the fact whether it separates with this solid substance or not.

We now take a liquid  $L_a$  (figs. 1—3) and we separate it by a semi-permeable membrane from an arbitrary liquid  $L_q$ . We shall say that  $L_a$  and  $L_q$  are in osmotic relation.

We now distinguish three cases.

1.  $L_q$  is situated on the isotonic curve  $a n$ .

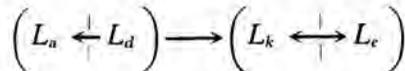
As  $L_a$  and  $L_q$  have, therefore, the same  $O.W.A.$ , no water shall diffuse from the one liquid to the other.

2.  $L_q$  is situated within the field  $a n W w$ .

As  $L_a$  now has a greater  $O.W.A.$  than  $L_q$ , water shall diffuse from  $L_q$  towards  $L_a$ ; this diffusion continues till the  $O.W.A.$  of both liquids becomes equal, consequently till they reach the same isotonic curve. As we have seen in the previous communication, it depends on the ratio of the quantities of  $L_a$  and  $L_q$  which curve this shall be. When we take for  $L_q$  f. i.  $L_d$  of fig. 1, then  $L_a$  may pass into  $L_k$  and  $L_d$  into  $L_c$ . Then the line  $e k$  must go through the point, which represents the complex of the original liquids  $L_a$  and  $L_d$ . In order to represent plainly the conversion, above-mentioned, we shall represent two liquids  $L_a$  and  $L_d$  which are in osmotic relation by:



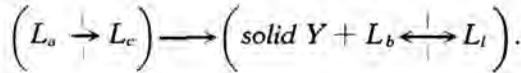
in which the little arrow indicates the direction in which the water diffuses. We now may represent the conversion by:



in which the double arrow indicates that the liquids  $L_k$  and  $L_c$  are in osmotic equilibrium.

3.  $L_q$  is situated within the field  $a n X v$ .

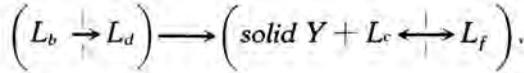
As  $L_a$  now has a smaller  $O.W.A.$  than  $L_q$ , water shall diffuse from  $L_a$  to  $L_q$ . When we take for  $L_q$  f. i.  $L_c$  of fig. 1, then the conversion becomes:



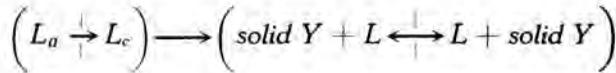
This means, therefore, that  $L_a$  gives water to  $L_c$  by which  $L_a$  passes into solid  $Y + L_b$  and  $L_c$  into  $L_l$ . The line  $gl$  will have to go now through the point, which indicates the complex of the original liquids  $L_a$  and  $L_c$ .

The result of the membrane-diffusion between the two liquids  $L_a$  and  $L_q$  is, therefore, different, according to the point  $L_q$  being situated, on-, at the left- or at the right of the isotonic curve  $an$ .

We will yet indicate some conversions, which the reader may easily deduce from the figures. We find f. i. from fig. 2:

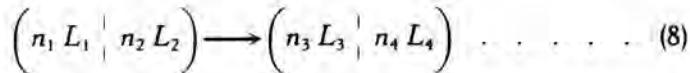


From fig. 3 is found a. o.:



in which  $L$  represents a saturated liquid between  $a$  and  $c$ . Consequently the result of the membrane-diffusion is here, that on both sides of the membrane the solid substance  $Y$  is separated and that the liquid on both sides of the membrane gets the same composition. The liquids  $L_b$  and  $L_e$ ,  $L_w$  and  $L_c$  etc. should give the same result.

We bring  $n_1$  quantities of  $L_1$  in osmotic relation with  $n_2$  quantities of  $L_2$ ; we assume that those  $n_1$  quantities of  $L_1$  pass into  $n_3$  quantities of  $L_3$  and those  $n_2$  quantities of  $L_2$  into  $n_4$  quantities of  $L_4$ . We may write this conversion:



in which the arrows which indicate the direction of the diffusion, are omitted. When we represent the composition of  $L_1 L_2$  etc. by  $x_1 y_1, x_2 y_2,$  etc., then are valid the equations:

$$n_1 x_1 = n_3 x_3 \qquad n_2 x_2 = n_4 x_4 \dots \dots \dots (9)$$

$$n_1 y_1 = n_3 y_3 \qquad n_2 y_2 = n_4 y_4 \dots \dots \dots (10)$$

$$n_1 + n_2 = n_3 + n_4 \dots \dots \dots (11)$$

The two equations (9) express that the quantity of the substance  $X$  rests unchanged as well at the one side as at the other side of the membrane, the two equations (10) express the same for the substance  $Y$ .

Equation (11) indicates, in connection with the equations (9) and (10) that the total quantity of water does not change with the diffusion. Consequently we have five equations for the definition of the six variables in the second part of (8). We find a sixth equation by the expression that  $L_3$  and  $L_4$  are in osmotic equilibrium, so that they are situated on the same osmotic curve.

Let us take the special case that  $L_1$  and  $L_2$  are situated with point  $W$  on a straight line, f. i.  $L_1 = \text{liquid } d$  and  $L_2 = \text{liquid } l$  from fig. 1. On both sides of the membrane now a same liquid arises, f. i. the liquid  $e$  (fig. 1) which we shall represent by  $L$ . Inversion (8) now passes into:

$$\left( n_1 L_1 \mid n_2 L_2 \right) \longrightarrow \left( n_3 L \mid n_4 L \right).$$

When we give to  $L$  the composition  $xy$ , then (9)–(11) pass into:

$$\begin{aligned} n_1 x_1 &= n_3 x & n_2 x_2 &= n_4 x \\ n_1 y_1 &= n_3 y & n_2 y_2 &= n_4 y \\ n_1 + n_2 &= n_3 + n_4. \end{aligned}$$

Herein is, as  $L_1 L_2$  and  $W$  are situated on a straight line:

$$x_1 : y_1 = x_2 : y_2.$$

The composition  $xy$  of liquid  $L$  and the quantities  $n_3$  and  $n_4$  of this liquid, which is on both sides of the membrane, are, therefore, defined. We find:

$$\begin{aligned} n_3 &= \frac{n_1 x_1 (n_1 + n_2)}{n_1 x_1 + n_2 n_2} = \frac{n_1 y_1 (n_1 + n_2)}{n_1 y_1 + n_2 y_2} \\ n_4 &= \frac{n_2 x_2 (n_1 + n_2)}{n_1 x_1 + n_2 x_2} = \frac{n_2 y_2 (n_1 + n_2)}{n_1 y_1 + n_2 y_2} \end{aligned}$$

and also:

$$\begin{aligned} n_3 : n_4 &= n_1 x_1 : n_2 x_2 = n_1 y_1 : n_2 y_2 \\ x &= \frac{n_1 x_1 + n_2 x_2}{n_1 + n_2} & y &= \frac{n_1 y_1 + n_2 y_2}{n_1 + n_2}. \end{aligned}$$

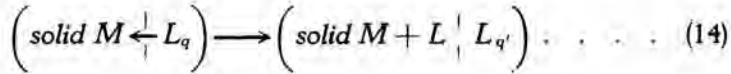
We bring a liquid  $L_q$  in osmotic relation with a mixture  $M$  of solid substances. When water is diffusing from  $L_q$  to the solid substances, then we shall represent it by:

$$\left( \text{solid } M \leftarrow L_q \right); \dots \dots \dots (12)$$

when nothing takes place, then we shall represent it by:

$$\left( \text{solid } M \mid L_q \right) \dots \dots \dots (13)$$

In order to define which of both these cases shall occur, we imagine that an infinitely small quantity of water diffuses from  $L_q$  towards the solid substances. A liquid  $L$  now arises of absolutely defined composition and changes into a liquid  $L_q'$  which differs infinitely little from  $L_q$ . The inversion is, therefore:



When  $L$  has a greater *O.W.A.* than  $L_q$ , then still more water shall diffuse to the solid substances; then we have a system (12). When, however,  $L$  has a smaller *O.W.A.* than  $L_q'$  then the water shall return again to  $L_q'$ ; consequently inversion (14) cannot take place, we have, therefore, a system (13).

Consequently it is dependent on the *O.W.A.* of liquid  $L$  whether the solid substances may be able to remove water from the liquid  $L_q$  or not. For this reason we will say:

the osmotic water-attraction of a solid substance or of a mixture of solid substances is the *O.W.A.* of the liquid, which arises when a very small quantity of water is added to this substance.

Consequently when we bring the component  $Y$  in osmotic relation with a liquid  $L$ , then it depends on the *O.W.A.* of liquid  $L_w$  (figs. 1—3), what will happen. As all liquids of curve  $w m$  have the same *O.W.A.* as  $L_w$  and, therefore, also as the solid component  $Y$ , we shall call this curve: curve (*O.W.A.* =  $Y$ ).

Further we shall say that a liquid, situated in the field  $w m W$ , is situated closer to  $W$  than curve (*O.W.A.* =  $Y$ ); of the other liquids we shall say that they are situated further from  $W$  than this curve.

We now easily find:

the component  $Y$ , in osmotic relation with a liquid, which is situated closer to  $W$  than curve (*O.W.A.* =  $Y$ ) shall remove water from this liquid;

the component  $Y$ , in osmotic relation with a liquid, which is situated further from  $W$  than curve (*O.W.A.* =  $Y$ ), cannot remove water from this liquid.

Consequently when we bring solid  $Y$  in osmotic relation with one of the liquids  $L_l$  (fig. 1),  $L_a$  or  $L_f$  (fig. 2) than nothing takes place. Reversally, when we bring one of these liquids in osmotic relation with  $L_w$ , the latter with separation of solid  $Y$ , shall lose its water totally or partially.

When we bring solid  $Y$  in osmotic relation with liquid  $L_d$  (fig. 1) or  $L_h$  (fig. 2) then water shall diffuse towards the solid substance; then either solid  $Y + L_w$  is formed or an unsaturated solution.

As a special case of the previous considerations follows at once which

shall take place when a binary liquid, containing the components  $W$  and  $X$ , is brought in osmotic relation with a new solid substance  $Y$ .

When this liquid is situated between  $m$  and  $X$  (figs. 1—3) then nothing takes place; when it is situated between  $W$  and  $m$ , then the solid substance  $Y$  shall remove water from this liquid; then either  $Y + L_w$  or an unsaturated solution of  $Y$  in water is formed.

*Leiden.*

*Lab. of Inorg. Chemistry.*

*(To be continued).*

**Physics.** — “*The Brownian Movement of a Thread*”. By A. HOUDIJK and Prof. P. ZEEMAN.

(Communicated at the meeting of November 29, 1925).

In an address on “Experimentell nachweisbare, der üblichen Thermodynamik widersprechende Molekularphänomene” delivered at the 84. Versammlung deutscher Naturforscher und Aerzte in 1912<sup>1)</sup> VON SMOLUCHOWSKI treats many phenomena that have been known for a long time (Brownian movement, opalescence of gases in the critical state, oscillation of the gas density about a normal middle value) seen from one point of view.

According to the kinetic theory the condition of an isolated system oscillates about a normal state, and can even very far depart from it under definite circumstances, in consequence of which the phenomena in question ensue.

The conditions through which a system in equilibrium passes, correspond to a canonical distribution, and the chance to a definite system defined by the coordinates  $p$  and the moments  $q$  is:

$$dW = ae^{-\frac{N}{RT}E} dq_1 dq_2 \dots dp_1 dp_2 \dots dp_n$$

in which  $E$  is the total energy.

On integration with respect to all the variables except  $\varepsilon$  (identical with a  $q$ ) which determines the deviation of the system, the number of systems at a definite moment with an  $\varepsilon$  lying between  $\varepsilon$  and  $\varepsilon + d\varepsilon$ , is:

$$dW = ce^{-\frac{N}{RT}\chi(\varepsilon)} d\varepsilon \dots \dots \dots (1)$$

This well-known equation — BOLTZMANN's exponential law — is characteristic of the kinetic theory. It indicates how far in consequence of the unordered thermal movement a parameter of a system departs from the value corresponding to stable equilibrium.

VON SMOLUCHOWSKI gives several applications, and treats two of them referring to the deformation of a solid body, which differ, therefore, from the known phenomena of variation of the parameter through the molecular motion.

<sup>1)</sup> M. v. SMOLUCHOWSKI, Phys. Zeitschr. 13, 1912 (1069).

One of them, the subject of our experimental investigation <sup>1)</sup> is the displacement of the lower end of a thin thread hanging vertically.

Any departure from the state of equilibrium will have the same probability. The factor  $a$  in formula (1) is, therefore, constant. Besides — since we are concerned with gravity and with elastic forces — the work done on a displacement from the state of equilibrium, is a quadratic function of the coordinates, so that we, therefore, get a distribution of deviations according to GAUSS's law of errors.

The strict calculation of the case is complicated, for the very reason that besides the work of gravity, also the work required for the bending should be considered.

The order of magnitude of the mean deviation is, however, also obtained when the thread is conceived as a rod, and only gravity is taken into account.

The mean displacement of the end of the thread becomes:

$$\sqrt{\delta^2} = \sqrt{\frac{RT}{N} \frac{2}{\pi a^2 \varrho g}}$$

in which  $a$  is the radius of the cross-section of the thread, and  $\varrho$  the density of the substance used.

This formula may also be derived by another way.

The difficulties met with in the experimental investigation, are among others radiometric phenomena and vibrations of the ground.

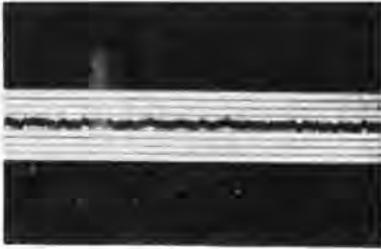
In main lines the arrangement was as follows.

The thread attached at one end, was placed in a small tray covered at the front and at the backside by a cover-glass. The free end of the thread was projected on the slit of a falling plate outfit, as is used among others to record electro-cardiograms. A PHILIPS Tungsten arc-lamp with an object glass as condenser serves for the illumination; for the projection is used a microscope with horizontal tube, provided with an apochromatic object glass and a compensation-eyepiece. The whole apparatus stands on a free-stone plate, attached to three free-stone pillars which are mounted on one of the heavy concrete floors of the physical laboratory "Physica". These floors weigh  $\pm 250.000$  kg., and rest — clear of the building — on a great number of poles driven in deep. Moreover, the observations were made in the night, between 1.30 and 3.30 a. m., after it had been ascertained that the movement of the floor has a large period only then. With a diaphragm the smallest quantity of light possible for the projection was transmitted.

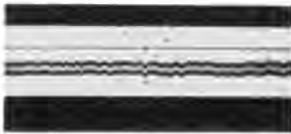
For a long time observations were also made in the hall of the country-

<sup>1)</sup> This investigation, in progress for a long time already, is mentioned in:  
 A. EINSTEIN. Untersuchungen über die Theorie der "Brownsche Bewegung". OSTWALD's Klassiker N<sup>o</sup>. 199. Anmerkung 15. 1922.  
 M. V. SMOLUCHOWSKI. Abhandlungen über die Brownsche Bewegung und verwandte Erscheinungen. OSTWALD's Klassiker N<sup>o</sup>. 207. Anmerkung 30. 1923.

house of one of us at Huis-ter-Heide, and a few times in the cellar of a house at Zeist. In a nightly observation at Huis-ter-Heide, made by one of us, the deviations of the end of the thread were directly observed, and the magnitude estimated by the eye piece micrometer. Many observations were made in the older physical laboratory, where the apparatus was mounted on a much smaller block of concrete.



Platinum 1  $\mu$ .



quartz 2  $\mu$ .

Further details and results will be given in the thesis for the doctorate of A. HOUDIJK, to be published later.

In the experiments the photographs are, of course, obtained with the thread vertical.

Wherever the investigation was performed, it was always found that the aspect of the phenomenon was the same.

The subjoined pictures give an idea of the photographs obtained.

The measurements were made with the microphotometer, and visually by enlarging the image.

The results, both of the last-mentioned measurement and those of the above-mentioned direct estimation, are in good agreement with the formula derived above.

The investigation was made with threads of different materials and different cross-sections.

**Geology** — "*The tectonics of the central part of the Sierra de los Filabres (South-Spain)*". By H. A. BROUWER and C. P. A. ZEYLMANS VAN EMMICHOVEN.

(Communicated at the meeting of November 29, 1924).

In his outlines of the geology of Spain R. DOUVILLE<sup>1)</sup> writes: "Au point de vue tectonique la chaîne bétique est encore inexplorée". The following will be for the main part a short review of results concerning the tectonics of the Sierra de los Filabres<sup>2)</sup>. Till now the admitted stratigraphic division was:

1. Crystalline schists of prae-triassic age.
2. Limestones, shales, slates and phyllites, rauchwackes, gypsum and dolomites, which in analogy with fossil-bearing sediments in the Sierra de Gádor were considered as being triassic.
3. Tertiary and more recent sediments.

We can add to this that also at different places of the Sierra de los Filabres typical triassic fossils (i.a. *Myophoria*) have been found (west of the hamlet La Yedra; south of the Menas-mines; in the Barranco del Pozo de la Nieve and west of the Tetica de Bacares). Whether really all crystalline schists are of prae-triassic age, can here be left out of discussion just as an exact determination of the stratigraphy of the trias — though these facts are of great importance for the tectonics — our first intention being to give only a general idea of the tectonic features. Among the crystalline schists garnetiferous micaschists are predominating; in some horizons they are alternating with many metamorphic igneous rocks (serpentine, amphibolites, gneisses). In other parts they consist only or nearly only of micaceous marbles.

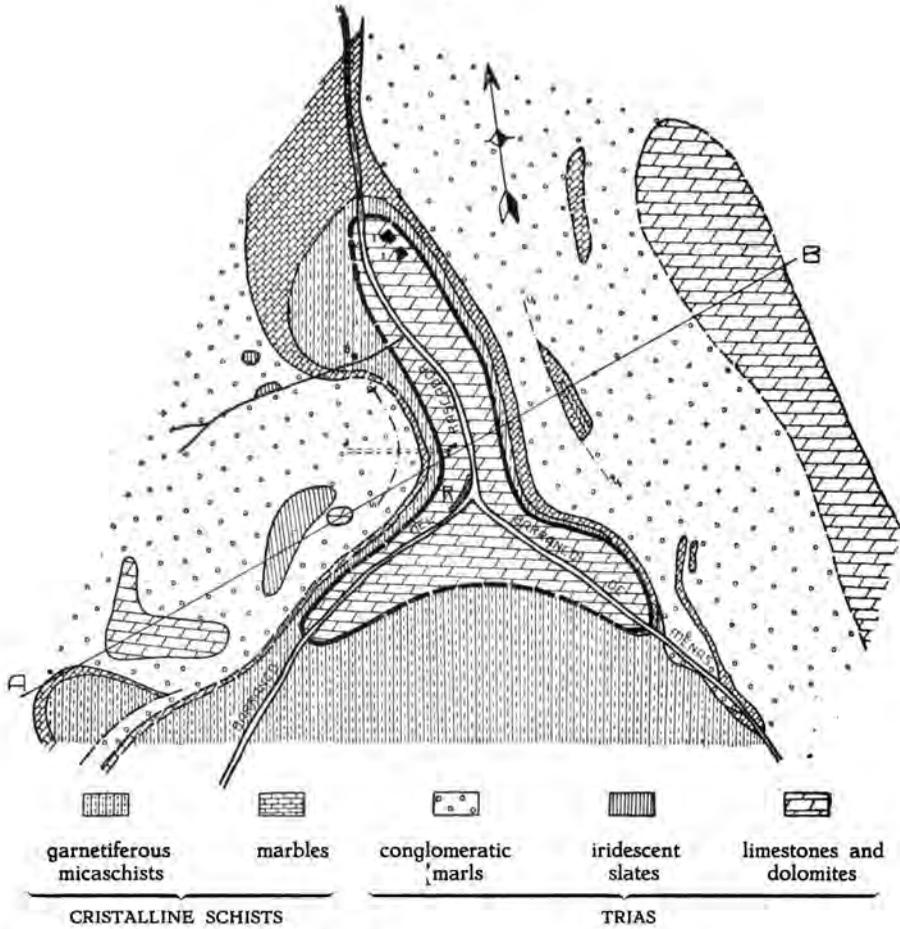
#### THE POST-TRIASSIC, PRAE-PLIOCENE TECTONICS IN CROSS-SECTION.

The Sierra de los Filabres belongs with its western prolongation, the Sierra Nevada, to the tertiary mountains, which can be followed in W.S.W.-E.N.E. direction from Gibraltar to Alicante. In the northern

<sup>1)</sup> R. DOUVILLE. La Péninsule Ibérique A. Espagne. Handbuch der Regionalen Geologie. Heft 7.

<sup>2)</sup> The investigations, of which here a review is given, commenced during an excursion led by H. A. BROUWER and R. W. VAN DER VEEN. These initiated more detailed studies by C. P. A. ZEYLMANS VAN EMMICHOVEN, one of the participants of this excursion.

Fig. 1.



garnetiferous  
micaschists

marbles

conglomeratic  
marls

iridescent  
slates

limestones and  
dolomites

CRISTALLINE SCHISTS

TRIAS

— — — — — outcrop overthrustplane.

..... faults

R El Rascador.

Scale 1 : 15.000.

**WINDOW OF EL RASCADOR.**

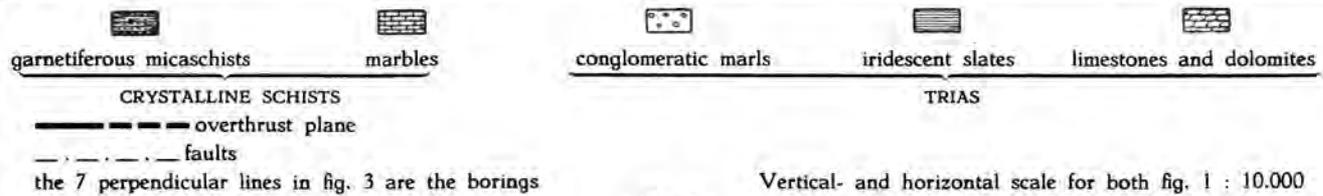
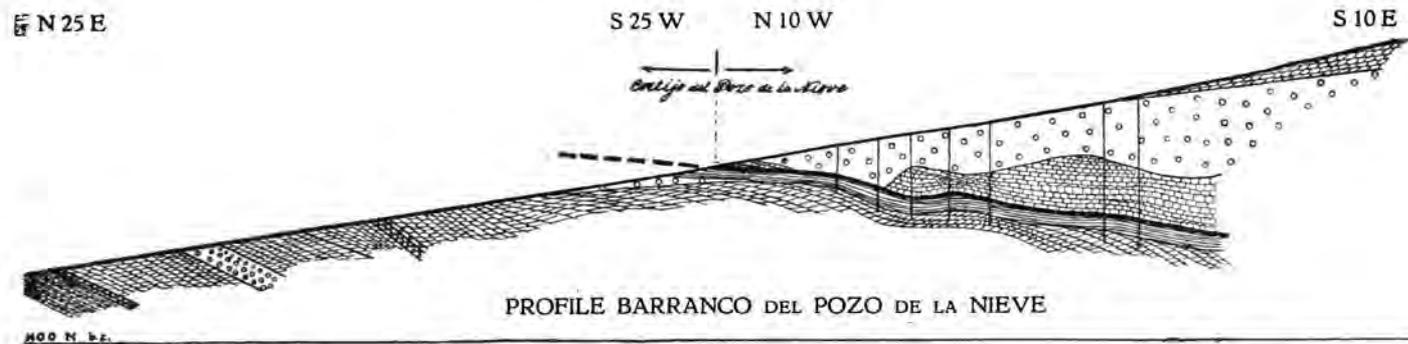
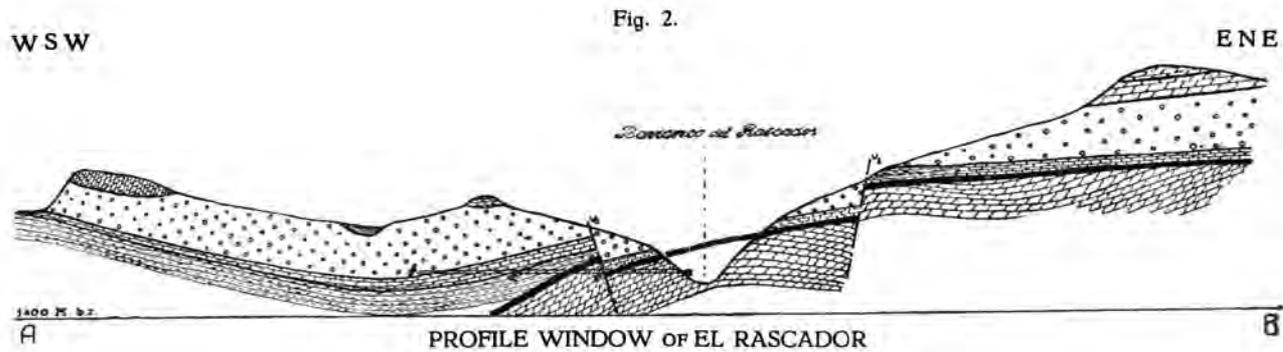


Fig. 3.

Vertical- and horizontal scale for both fig. 1 : 10.000

subbetic mountains DOUVILLE<sup>1)</sup>, NICKLES<sup>2)</sup> and GENTIL<sup>3)</sup> have pointed out the existence of large overthrusts which show movements to the N. and N.N.W. From the following will appear that the structure of the betic mountains in the central part of the Sierra de los Filabres shows characteristics, which likewise point out important horizontal movements in N. and N.W. direction. These facts fit in the general scheme of structure of the Alps of which the betic ranges may be considered to be the direct western continuation.

Of our observations, which prove the existence of large overthrusts in the Sierra de los Filabres, the most important are :

*The window ("Fenster") of El Rascador. (Figs. 1 and 2.)*

At the confluence of the Barranco del Rascador and the Barranco de Menas the bottom of the valley consists of triassic limestones. As well down-river as up the stream at a distance of about 500 M. from the confluence these triassic limestones dip under cristalline schists which here are for the greater part marbles, with some garnetiferous micaschists.

The triassic-limestones show strong pressure-phenomena near the abnormal contact-plane, while the superposed garnetiferous micaschists have also been strongly squeezed out. The abnormal contact-plane between these two places can also be followed along the slopes of the two barrancos, especially at the east-side. So we find here a window of triassic limestones in the cristalline schists. On top of the latter lie again triassic sediments, consisting of conglomeratic marls, rauchwackes, limestones and dolomites.

*Borings S. of the Cortijo del Pozo de la Nieve. (Fig. 3.)*

In the upper course of the Barranco del Pozo de la Nieve at a distance of more than 1.5 K.M. east of the window of El Rascador, W. F. C. ENGELBERT VAN BEVERVOORDE, mining-engineer of the Sociedad Minera Cabarga y San Miguel, brought down a series of borings in a line with an almost S.-N. direction.

The results are given in the S. part of profile fig. 3.

1) R. DOUVILLE. Esquisse géologique des Pré-alpes subbétiques (Partie Centrale). Thèse de doctorat. 1906.

2) R. NICKLES. Sur l'existence des phénomènes de charriage en Espagne dans la zone subbétique. Bull. de la Soc. géol. de France. 4e série, IV, p. 223, 1904.

3) L. GENTIL. Sur l'existence de grandes nappes de recouvrement dans la province de Cadix. Comp. Rend. des Sc. de l'Acad. des Sc. CLXVI, p. 1003, 1917.

Id. Sur l'existence en Andalousie des nappes de recouvrement de la province de Cadix id. CLXVII, p. 83, 1918.

Id. Sur l'origine des nappes de recouvrement de l'Andalousie. id. p. 238, 1918.

Id. Sur l'âge des nappes de recouvrement de l'Andalousie et sur leur raccordement avec les nappes préifaines (Maroc. septentrional) id. p. 373, 1918.

Here we see a 75 M. thick deposit of marbles rather suddenly thinning out to the N., extending under a thick series of conglomeratic triassic marls and rauchwackes, followed by about 20 M. of strata which produced in the boring-samples a clay of a light-blue colour. Thereafter the borings yielded intensively folded triassic limestones. After having perforated a thickness of 80 M. of these limestones the borings were stopped.

These observations were completed by the profile in the near valley.

Going from S. to N. we found :

Conglomeratic trias-marls and rauchwackes.

Crystalline schists, for the greater part consisting of marbles. (Undistinct outcrops).

Triasslates, about 20 M.

Trias-limestones (very thick).

Conglomeratic trias-marls 90 c.M.

Crystalline schists (75 c.M. marble on top of garnetiferous micaschists).

Between this abnormal succession and the one of the window of El Rascador exists this difference that the  $\pm$  20 M. layer of triassic slates in the profile of the borings was not found in the window.

#### STRIKES AND FRACTURES.

In describing the tectonics in the direction of the folding axes we mention in the first place the complicated structures originated at greater depths during the older tertiary phases of mountain-building, and afterwards uncovered by erosion. Of the newer phases we don't know these complicated structures at greater depths, but only the major relief-features and the movements along fractures. This distinction is not made to make a sharp division between certain periods of intense mountain-building, but because only in this way we are able to give a concise description of the structure of the mountain chain.

#### *Post-triassic, prae-pliocene strikes.*

North of a line of E.-W. direction over Macael, which we will describe later as a striking longitudinal fracture-line, we do not find any sediments older than of triassic age. In these triassic sediments the strikes have a S.W.-N.E. direction. South of this line the strikes of the trias are on the whole strongly variable, but in some parts the general direction of strike can be well defined. At both sides of the upper-course of the Barranco del Rascador we find S.W.-N.E. directions, farther to the east the strike is generally E.-W., which still farther eastward in the vicinity of the Calar de Layón, is distorted to a N.W.-S.E. direction. Proceeding to

the E. the strike gradually approaches its former E.-W. direction. For the sake of brevity these tectonics will be called the tertiary tectonics.

*The youngest tectonics.*

Young-tertiary and quaternary sediments cover unconformably the older ones along the northern border of the mountain range. The trend of these strata is more or less E.-W., the dips amount to an average of about 30° to the north; dips to the south are likewise to be found.

Concerning the horizontal projection of the geanticlinal axis of the present mountain-chain, can be said, that it cannot be stated with certainty where the strongest recent uplift has taken place, because the topography has been influenced by erosion. We can state though, that there are deviations from the general E.-W. trend of the mountain-chain; the horizontal projection of the geanticlinal axis shows a few bending-points and near these bending-points important transversal fractures are found, just as occurs between the Sierra Nevada and the Sierra de Los Filabres on a larger scale.

These *transversal fractures* are from E. to W.:

1. a system of S.S.W.-N.N.E. fractures, S.E. of Macael;
2. the fracture of the Rio de Bacares, likewise with a S.S.W.-N.N.E. direction;
3. the S.W.-N.E. trending fractures of the Ríos del Fargali and de las Herrerías. It is of importance that the fracture-lines stated sub 2 and 3 are situated at both sides of the E.-W. strikes in the trias, mentioned with the tertiary tectonics, so thus — at any rate this being the case with the eastern ones — in the vicinity of a bending-point of the tertiary strike. The transverse fractures, along which sometimes a horizontal movement is clearly evident, are the expression near the surface of similar movements with horizontal differences of velocity as those, which formed the distortions of the tertiary strikes at greater depths.

Of the *longitudinal fractures*, which are also of much importance for the youngest tectonics, the most obvious is the great E.-W. directed fracture-line, which can be followed in a western direction from Macael till S.W. of Serón. Along this fracture-line the southern part is relatively upheaved, the dip of the fractures plane is steep and often to the south; so we see, that also the youngest tectonics show evidences of reversed faulting in a northern direction.

Thus the transversal as well as the longitudinal fractures show characteristics, from which an analogy between the recent orogenetic movements, and those, by which the tertiary tectonics were formed, is evident.

THE PRAE-TRIASSIC TECTONICS AND THEIR DEFORMATION BY  
THE POST-TRIASSIC MOVEMENTS. (Fig. 4).

The prae-triassic tectonics show to the north of the plain of the Guadalquivir, where younger mountain-building movements did not take place, a

distinct more or less N.W.-S.E. strike. These hercynic strikes are cut off under a sharp angle by the important W.S.W.-E.N.E. trending fault, confining the young basin of the Guadalquivir to the north. In the subbetic chains prae-triassic sediments are not uncovered, but in the betic mountains sediments, showing evidences of the hercynic orogenetic forces are again exposed.

It is important, that the same N.W.-S.E. strikes of the prae-triassic sediments are found in the Sierra de los Filabres. In this mountain-chain we see a part of the direct S. E. continuation of the hercynic structures of the Sierra Morena. Still farther south in the Sierra de Alhamilla the same strikes are found to be predominant in the crystalline schists<sup>1)</sup>.

The subbetic and betic mountains were formed by the younger Alpine movements with a W.S.W.-E.N.E. strike, cutting the direction of the hercynic mountains obliquely.

In the Sierra de los Filabres the influence of the younger movements on the ancient strikes is clearly to be determined. Although the ancient hercynic strike in prae-triassic sediments has mostly disappeared by the new orientating influence of the post-triassic movements, the hercynic strikes can still be followed with the aid of petrographically characteristic strata. If we follow f.i. zone of marbles in the crystalline schists, than we see it extending in a northwestern direction from the Barranco de Sobrino till N.W. of the window of El Rascador. Thereafter the zone bends in a western direction, this even being a W.S.W. one for a short distance west of the Barranco del Fargalí, to take from there to the west, till past Alcóntar, gradually the old hercynic (N.W.-S.E.) strike of the Sierra Morena.

This deviation from the hercynic strike, shown by the zone of marbles, can be brought in direct relation with the bending of the tertiary strike, as this has been mentioned above for the triassic sediments south of the longitudinal fracture-line Macael-Serón.

Bearing in mind that the bending of the tertiary strikes is due to differences in velocity of horizontal movements at greater depth, then these differences of velocity will have altered also the strike of the zones of similar petrographic composition in the crystalline schists.

Assuming an originally N.W.-S.E. directed hercynic strike and a W.N.W.-E.N.E. direction of the strikes during the primary phases of the Alpine mountain-building, deformations of the hercynic and those of the original younger strikes turn out to be caused by the same differences of velocity of the mountain-building movements, which is clearly shown in fig. 4.

We draw therefore the conclusion, that the hercynic mountains have continued from the Sierra Morena in a southeastern direction into the

<sup>1)</sup> W. H. HETZEL. Bijdrage tot de geologie van de Sierra Alhamilla. Proefschrift 1923. 's-Gravenhage.

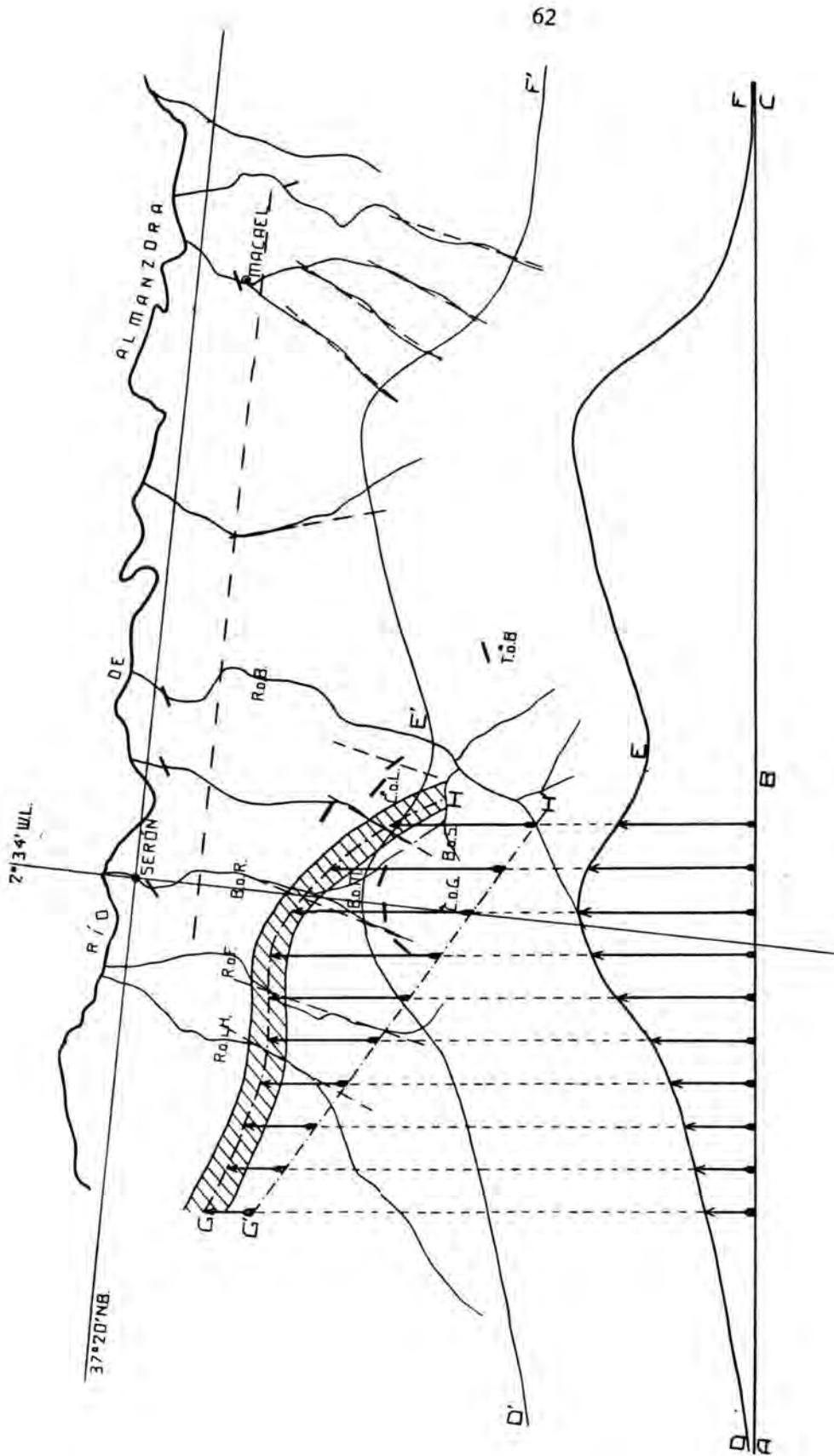


Fig. 4.

Scale 1 : 200,000

## EXPLANATION OF FIGURE 4.

*The deformation of the prae-triassic tectonics by the post-triassic movements.*

-  zone of marbles in the crystalline schists.
- — — faults.
- tertiary strikes in the trias.
- A B C direction of the geanticlinal axis if no differences in velocity of the horizontal movements had taken place.
- D E F approximate form of the present geanticlinal axis.
- D' E' F' is D E F displaced to the north.
- G' H' supposed hercynic direction of the zone of marbles.
- |                                   |                                       |
|-----------------------------------|---------------------------------------|
| R. d. l. H. Rio de las Herrerias. | R. d. B. Rio de Bacares.              |
| R. d. F. Rio del Fargali.         | C. d. G. Calar de Gallinero 2050 M.   |
| B. d. R. Barranco del Rascador.   | C. d. L. Calar de Layón 1980 M.       |
| B. d. M. Barranco de Menas.       | T. d. B. Tetica de Bacares 2081.40 M. |
| B. d. S. Barranco de Sobrino.     |                                       |

Mediterranean region. So we see here a great difference between the directions of the younger and the ancient mountains, an analogon of which are the hercynic relict-structures as they were described in Stiria by Heritsch<sup>1)</sup>).

<sup>1)</sup> FR. HERITSCH. Die Grundlagen der alpinen Tektonik. Berlin. GEBR. BORNTRAEGER 1923, p. 14.

**Chemistry.** — "*The optically active components of chlorosulphoacetic acid*". By H. J. BACKER and W. G. BURGERS. (Communicated by Prof. F. M. JAEGER.)

(Communicated at the meeting of January 31, 1925).

The failure of various attempts to resolve racemic chlorosulphoacetic acid  $\text{SO}_3\text{H} \cdot \text{CHCl} \cdot \text{CO}_2\text{H}$  by the usual methods suggested some doubt as to the applicability of the theory of asymmetric carbon to simple compounds <sup>1)</sup>.

Preliminary observations on its resolution <sup>2)</sup> were not confirmed by POPE and READ, who then succeeded in the resolution of another simple compound, namely chloriodomethanesulphonic acid <sup>1)</sup>.

Supposing that the failures might be caused by racemisation, we have attempted the resolution by "cold crystallisation" of alkaloidal salts. This method indeed succeeded.

The ammonium or sodium salt of chlorosulphoacetic acid was treated in aqueous solution with two molecules of the acetate or phosphate of strychnine.

The dilution was chosen so, that only a small part of the strychnine salt, about one fifth, crystallised. Decomposed by ammonia at 0°, it gave an active, dextrorotatory ammonium salt.

For purification of the strychnine salt, the same "cold crystallisation" was applied. Accordingly it was decomposed by ammonia and in a suitable dilution again treated with the acetate of strychnine. In this way it could be ascertained when the maximum value of the rotation was attained.

Decomposition of the ammonium salt by sulphuric acid gave the dextrorotatory acid.

The laevo-component was obtained in the same way by means of cinchonine.

The following values of the molecular rotatory power were found :

Wavelength $\lambda$ ( $\mu\mu$ )	589	533	494
Chlorosulphoacetic acid [M]	39°	50°	62°
Neutral ammonium salt [M]	20°	26°	34°

The active acids and salts racemise slowly at room temperature. On evaporation on a water-bath the solutions lose their activity completely. In alkaline solution the salts are quickly racemised.

A detailed account of this research will appear in the „Journal of the chemical Society of London”.

*Organic Chemical Laboratory of the University.*

*Groningen, January 1925.*

<sup>1)</sup> POPE and READ, Journ. chem. Soc. **93**, 794 (1908); **105**, 811 (1914).

<sup>2)</sup> PORCHER, Bull. Soc. chim. (3) **27**, 438 (1902).

**Chemistry.** — "*Optical resolution of bromosulphoacetic acid*". By H. J. BACKER and H. W. MOOK. (Communicated by Prof. F. M. JAEGER.)

(Communicated at the meeting of January 31, 1925).

The resolution of chlorosulphoacetic acid, described in the preceding communication, led us to attempt the application of the same method to an analogous asymmetric compound, namely bromosulphoacetic acid,  $\text{SO}_3\text{H} \cdot \text{CHBr} \cdot \text{CO}_2\text{H}$ .

Sodium bromosulphoacetate gives in the cold crystalline salts with various alkaloids, dissolved in dilute acetic acid. These salts were examined polarimetrically after careful decomposition with ammonia and elimination of the alkaloid.

Strychnine and cinchonidine gave a dextrorotatory ammonium salt, whilst brucine, chinidine and yohimbine led to the laevocompound. Cinchonine gave variable results.

Strychnine and brucine proved to be the most suitable alkaloids for preparing both enantiomorphs in a pure state.

The *dextrorotatory acid* was prepared from 40 m.mol. sodium bromosulphoacetate and 80 m.mol. acetate of strychnine in a dilution of 2100 c.c. After a day one fifth of the total amount had crystallised.

The product was decomposed with ammonia and treated with strychnine in acetic solution in such dilution, that again only a part crystallised. The rotatory power of the ammonium salt had reached its maximum and was not changed by two further crystallisations.

Another method of controlling the optical purity of the strychnine salt consists in washing the finely powdered substance with water. The pure product did not change by this treatment, whilst the rotation of a less pure specimen, examined as ammonium salt, rose to the value of the pure salt.

As even a small excess of a strong base immediately causes racemisation, the d-barium salt was not prepared from the strychnine salt with baryta, but with barium iodide. The dextrorotatory acid, prepared both from the d-barium salt and from the d-ammonium salt with sulphuric acid, had double the rotation of the ammonium salt in the same dilution.

Brucine served for the separation of the *laevorotatory acid*.

As the solubilities of the brucine salts of the two enantiomorphs do not differ much, it appeared desirable to eliminate first a part of the dextro-compound by means of strychnine.

Thus from 20 m.mol. of *r*-bromosulphoacetic acid a fifth part was

separated as strychnine salt, and the mother liquor, decomposed by ammonia, was treated with the acetate of brucine in a dilution of 2 liters. One tenth part of the remaining acid crystallised as brucine salt.

This product, washed twice with 50 c.c. cold water, was pure and showed as ammonium salt the same rotation as the enantiomorph, in opposite direction.

The rotatory power of the l-acid, prepared from this ammonium salt with sulphuric acid, corresponded to that of the d-acid.

The highest constant values, found for the molecular rotation of the two active bromosulphoacetic acids and their neutral ammonium salts, are reproduced in next table :

$\lambda$ ( $\mu$ )	589	560	533	510	486
acid [M]	31°	37°	42°	47°	56°
salt [M]	16°	18°	21°	24°	27°.

Racemisation of acid and salt takes place slowly at room temperature. A dilute solution of the acid may be boiled for a few minutes without appreciable alteration.

Traces of strong bases greatly accelerate racemisation of the salts.

Experimental details of this research will be published elsewhere.

*Organic Chemical Laboratory of the University.*

*Groningen. January 1925.*

**Mathematics.** — "Grundzüge einer Theorie der Kurven". By Dr. K. Menger. (Communicated by Prof. L. E. J. Brouwer).

(Communicated at the meeting of January 31, 1925).

1. *Der Kurvenbegriff.* Durch keine der älteren Kurvendefinitionen wurde das, was in der Anschauung für die Kurven charakteristisch ist, restlos erfasst. Die Jordanschen "Kurven" (die eindeutigen stetigen Bilder der Strecke) und die irreduziblen Kontinua können bekanntlich ganze Flächenstücke enthalten, — zu den einfachen Kurvenbögen (den topologischen Bildern der Strecke) gehört schon eine so einfache Kurve, wie die Kreislinie, nicht, — und die Cantorsche Definition der ebenen Kurven als nirgends dichte Kontinua ist auf andre Euklidische Räume prinzipiell unübertragbar. Wir bezeichnen, gestützt auf eine allgemeine Dimensionstheorie<sup>1)</sup>, als Kurven die eindimensionalen Kontinua. Ein Kontinuum  $K$ , in dem (durch eine Metrik oder axiomatisch) Umgebungen definiert sind, heisst demgemäss Kurve, wenn zu jedem Punkt von  $K$  beliebig kleine Umgebungen mit diskontinuierlichen (d. h. keine Kontinua enthaltenden) Begrenzungen existieren. Die Dimensionstheorie lehrt, dass die Kurvennatur gegenüber topologischen Abbildungen invariant ist, — dass das Intervall des  $R_1$  und mithin jeder einfache Kurvenbogen eine Kurve ist, — dass dagegen im  $R_n$  ( $n \geq 2$ ) die Kurven nirgends dicht sind und im  $R_n$  ( $n \geq 3$ ) ein zusammenhängendes Komplement besitzen. Im  $R_2$  sind die Kurven mit den nirgends dichten Kontinua (also mit den Kurven im Cantorschen Sinn) identisch. Die Vereinigung abzählbar vieler Kurven ist eindimensional, also wenn sie ein Kontinuum ist, eine Kurve.

2. *Die Ordnung der Kurvenpunkte.* Jene Kurvenpunkte, zu welchen beliebig kleine Umgebungen mit endlichen Begrenzungen existieren, nennen wir *regulär*. Wenn zu einem regulären Punkt  $p$  eine natürliche Zahl  $n \geq 1$  existiert derart, dass es beliebig kleine Umgebungen von  $p$  gibt, deren Begrenzungen die Mächtigkeit  $n$  haben, und  $n$  die kleinste Zahl dieser Eigenschaft ist, dann sagen wir,  $p$  sei ein Kurvenpunkt der *Ordnung  $n$* <sup>2)</sup>. Die regulären Punkte, welche von keiner bestimmten endlichen Ordnung sind, nennen wir von *wachsender* Ordnung oder von der Ordnung  $w$ . Die nicht regulären Punkte einer separabeln vollständigen Kurve zerfallen in solche von der Ordnung  $\aleph_0$ , das sind jene Punkte, zu welchen beliebig kleine Umgebungen mit abzählbaren Begren-

<sup>1)</sup> Vgl. meine Arbeiten über die Dimension von Punktengen I Teil, Monatshefte f. Math. u. Phys. 1923, S. 148; II. Teil ebenda 1924, S. 137 und Proc. Ac. Amst. Vol. XXVII, p. 639, 1924, sowie die daselbst zitierten Schriften von L. E. J. BROUWER und P. URYSOHN.

<sup>2)</sup> Monatshefte 1923, S. 156.

zungen existieren, — und in Punkte von kontinuierlicher Ordnung oder der Ordnung  $c$ , das sind jene Punkte, für welche alle hinlänglich kleinen Umgebungen Begrenzungen von der Mächtigkeit des Kontinuums besitzen. — Man bestätigt leicht, dass die so definierte Ordnung eine topologische Invariante ist. — Ganz allgemein gilt ferner der Satz, dass die Menge aller Punkte des Raumes, zu welchen beliebig kleine Umgebungen von irgend einer bestimmten Eigenschaft existieren, ein  $G_\delta$  ist, d. h. Produkt von abzählbar vielen offenen Mengen. Bezeichnet  $K^\alpha$  ( $\alpha = 1, 2, 3, \dots, \omega, \aleph_0, c$ ) die Menge aller Punkte der Ordnung  $\alpha$  der Kurve  $K$ , so ergibt sich aus dem angeführten Satz in der Bezeichnungsweise von HAUSDORFF für die Borelschen Mengen das Schema:

$$\begin{array}{cccc}
 K^1, K^2, K^3, \dots, K^\omega, K^{\aleph_0}, K^c & & & \\
 \underbrace{G_\delta G_{\delta_\rho}} & \dots & \dots & \\
 \underbrace{G_\delta \quad G_{\delta_\rho}} & \dots & \dots & \\
 \underbrace{G_\delta} & \dots & \dots & \\
 \dots & & & \\
 \underbrace{G_{\delta_\sigma} \quad F_{\delta_\rho}} & \dots & & \\
 \underbrace{G_\delta \quad G_{\delta_\rho}} & & & \\
 \underbrace{G_\delta} & & & F_\sigma
 \end{array}$$

3. Die Endpunkte. Die Eigenschaften der Punkte erster Ordnung oder, wie wir auch sagen können, der Endpunkte einer Kurve  $K$  lassen sich in folgende leicht beweisbare Sätze zusammenfassen: In jeder total vollständigen Kurve (d.h. in jeder Kurve, deren sämtliche beschränkten Teile kompakt sind) liegen die Punkte von höherer als erster Ordnung dicht und bilden einen kondensierten, in jedem Punkt der Kurve eindimensionalen  $F_\sigma$ , der in jedem nicht leeren, offenen Teil der Kurve Kontinua enthält. Die Menge  $K^1$  der Endpunkte ist entweder leer oder null-dimensional, d. h. zu jedem Punkt von  $K^1$  existieren beliebig kleine Umgebungen mit zu  $K^1$  fremder Begrenzung. Jedenfalls ist  $K^1$  diskontinuierlich, doch kann  $K^1$  unter Umständen in  $K$  dicht liegen. Separabilität und Vollständigkeit von  $K$  vorausgesetzt, ist dies dann und nur dann der Fall, wenn die Menge  $K - K^1$  der Punkte von höherer als erster Ordnung — von erster Kategorie im Sinn von BAIRE, d.h. Summe abzählbar vieler in  $K - K^1$  nirgends dichter Mengen ist.<sup>1)</sup> Der letzte Satz ergibt sich auf Grund der Hausdorffschen Residuentheorie und des einfachen Satzes, dass in einem separablen vollständigen Raum die Mengen  $F_\sigma$ , welche mit ihrem Residuum übereinstimmen, identisch sind mit jenen von erster Kategorie.

<sup>1)</sup> In gewissem Sinn sind dann also die Endpunkte dichter angeordnet als die übrigen Kurvenpunkte.

4. *Die nicht regulären Punkte.* Ganz allgemein gilt der Satz, dass die Menge aller Punkte des Raumes, für die alle hinlänglich kleinen Umgebungen eine gewisse Eigenschaft  $E$  nicht besitzen, entweder leer oder ein kondensierter, in keinem seiner Punkte nulldimensionaler  $F_\sigma$  ist, der in jedem seiner nicht leeren, offenen Teile Kontinua enthält, — wofür über die Eigenschaft  $E$  vorausgesetzt wird, dass sie zugleich mit je zwei Umgebungen auch ihrer Summe, und zugleich mit einer Umgebung  $U$  auch jeder Umgebung, deren Begrenzung Teil der Begrenzung von  $U$  ist, zukommt. Angewendet auf die nicht regulären Punkte, ergibt dieser Satz (der auch der abstrakte Kern gewisser Sätze über die Struktur der  $n$ -dimensionalen Mengen ist), dass in jeder Kurve  $K$  die Menge  $K^\infty$  der nicht regulären Punkte und auch die Menge  $K^c$  der Punkte von kontinuierlicher Ordnung entweder leer ist, oder einen kondensierten, in jedem seiner Punkte eindimensionalen  $F_\sigma$  bildet, der in jedem seiner nicht leeren offenen Teile Kontinua enthält. Während die Punkte der Ordnung  $w$  isoliert liegen können, liegen also in einer Kurve, wenn sie einen einzigen nicht regulären Punkt enthält, ganze Kontinua von nicht regulären Punkten. Immerhin kann die Menge  $K^\infty$  von sehr einfacher Struktur, z. B. ein einfacher Kurvenbogen sein. Die Menge  $K^c$  dagegen ist auch selbst von der Ordnung  $c$  zumindest in allen jenen ihrer Punkte, in deren Nachbarschaft ihr Komplement  $K - K^c$  für jedes  $\varepsilon > 0$  mit einer Nullfolge von Umgebungen überdeckbar ist, deren Durchmesser  $< \varepsilon$  und deren Begrenzungen abzählbar sind, — insbesondere also <sup>1)</sup> in allen jenen ihrer Punkte, in deren Nachbarschaft die Menge  $K^c$  nicht bloss ein  $F_\sigma$ , sondern auch ein  $G_\delta$  ist.

5. *Zerlegungssätze.* Wir nennen halbkompakt eine Menge, die Summe abzählbar vieler kompakter Mengen ist. Damit zu jedem Punkt einer kompakten (halbkompakten) abgeschlossenen Menge  $M$  beliebig kleine Umgebungen einer gewissen Eigenschaft  $E$  existieren, ist notwendig und hinreichend, dass  $M$  für jedes  $\varepsilon > 0$  mit endlich vielen (mit einer Nullfolge von) Umgebungen  $< \varepsilon$  von der Eigenschaft  $E$  überdeckt werden kann. Wenn zugleich mit den Umgebungen  $U_1$  und  $U_2$  auch  $U_1 + U_2$  und  $U_1 - U_1 \cdot \bar{U}_2$ , (falls diese Menge nicht leer ist) und zugleich mit  $U$  jede Umgebung, deren Begrenzung Teil der Begrenzung von  $U$  ist, die Eigenschaft  $E$  besitzt und wenn ferner die Summe der Begrenzungen von abzählbar vielen Umgebungen mit der Eigenschaft  $E$  diskontinuierlich ist, dann ergibt sich auf Grund der sub 4 angeführten Struktursätze weitergehend: Notwendig und hinreichend dafür, dass zu jedem Punkt der kompakten (halbkompakten) abgeschlossenen Menge  $M$  beliebig kleine Umgebungen der Eigenschaft  $E$  existieren, ist, dass  $M$  für jedes  $\varepsilon > 0$  Summe von endlich vielen (einer Nullfolge von) abgeschlossenen Umgebungen der Eigenschaft  $E$  ist, deren Durchmesser  $< \varepsilon$  sind und die

<sup>1)</sup> Vgl. K. MENGER, Einige Ueberdeckungssätze der Punktmengenlehre, Wien. Ber. 1924 in Druck.

zu je zweien keinen inneren Punkt gemein haben. Diesem Satz zufolge sind die Kurven, bzw. die Kurven von höchstens abzählbarer Ordnung (d.h. die Kurven ohne Punkte der Ordnung  $c$ ), bzw. die regulären Kurven (d.h. die Kurven, die bloss reguläre Punkte enthalten), unter den kompakten Kontinua dadurch charakterisiert, dass sie für jedes  $\varepsilon > 0$  Summe endlich vieler abgeschlossener Umgebungen  $< \varepsilon$  sind, die zu je zweien diskontinuierliche, bzw. abzählbare, bzw. höchstens endliche Durchschnitte haben.

6. *Zusammenhang im kleinen.* Ein Kontinuum  $C$  heisst nach HAHN (Wien. Ber. 1914 S. 2434) zusammenhängend im kleinen im Punkt  $p$ , wenn für jedes  $\varepsilon > 0$  alle Punkte einer hinlänglich kleinen Umgebung von  $p$  mit diesem Punkt durch Teilkontinua von  $C$  verbindbar sind, deren Durchmesser  $< \varepsilon$  sind. Als Anwendung der oben angeführten abstrakten Sätze ergibt sich zunächst, dass die Menge aller Punkte, in denen  $C$  nicht zusammenhängend im kleinen ist, entweder leer ist oder einen kondensierten, in keinem seiner Punkte nulldimensionalen  $F_\sigma$  bildet, der in jedem seiner nicht leeren offenen Teile Kontinua enthält. Im kleinen zusammenhängend (schlechthin) heisst ein Kontinuum, das in jedem seiner Punkte im kleinen zusammenhängend ist. Unter den kompakten Kontinua sind nach HAHN die im kleinen zusammenhängenden identisch mit den Jordanschen "Kurven", d. h. mit den eindeutigen stetigen Bildern der Strecke. Wenn wir demnach die Kurven im Sinn unserer Definition, welche zusammenhängend im kleinen sind, charakterisieren, so haben wir damit zugleich unter den Jordanschen "Kurven" gerade jene herausgehoben, welche den Namen Kurven mit Recht tragen <sup>1)</sup>. Nun hatte SIERPIŃSKI (Fund. Math. I, S. 44) gefunden, dass unter den kompakten Kontinua für die Jordanschen Kurven auch charakteristisch sei, dass sie für jedes  $\varepsilon > 0$  Summe von endlich vielen Kontinua  $< \varepsilon$  sind. Für die im kleinen zusammenhängenden Kurven (im Sinn unserer Definition) ergibt sich nun eine Verschärfung der sub 5 angeführten Zerlegungssätze, welche durch einige Zusatzworte zur Sierpińskischen Charakterisierung der Jordanschen Kurven unter diesen letzteren die wirklich eindimensionalen aussondert: Notwendig und hinreichend, damit ein kompaktes Kontinuum  $K$  eine im kleinen zusammenhängende Kurve (= ein eindimensionales stetiges Bild einer Strecke), bzw. eine im kleinen zusammenhängende Kurve höchstens abzählbarer Ordnung, bzw. eine im kleinen zusammenhängende reguläre Kurve sei, ist, dass  $K$  für jedes  $\varepsilon > 0$  Summe von endlich vielen Kontinua  $< \varepsilon$  ist, die zu je zweien diskontinuierliche, bzw. abzählbare, bzw. höchstens endliche Durchschnitte haben.

7. *Die regulären Kurven.* Da jede Zerlegung eines kompakten Kontinuums in endlich viele abgeschlossene Umgebungen  $< \varepsilon$  mit zu je zweien

<sup>1)</sup> Speziell im  $R_2$  formulieren wir damit eine Bedingung für die Identität von Jordanschen und Cantorschen Kurven.

höchstens endlichen Durchschnitten auch eine Zerlegung zur Folge hat in endlich viele Kontinua  $< \varepsilon$  mit zu je zweien höchstens endlichen Durchschnitten, so sehen wir, dass jede reguläre Kurve zusammenhängend im kleinen ist. Darüber hinaus gilt der Satz, dass jede Kurve in jedem regulären Punkt zusammenhängend im kleinen ist. Aber die Menge der nicht regulären Punkte, in denen eine Kurve  $K$  zusammenhängend im kleinen ist, muss nicht leer sein; sie bildet einen  $F_{\sigma, \varepsilon}$ , der auch Punkte von  $K^c$  enthalten kann. Es existieren sogar nicht reguläre Kurven, die in jedem ihrer Punkte zusammenhängend im kleinen sind, und nicht reguläre Kurven, die nebst allen Teilkurven in einem irregulären Punkt im kleinen zusammenhängend sind. Andererseits gibt es reguläre Kurven, die Häufungskontinua, d.h. nirgends dichte Teilkurven enthalten. Doch lässt sich vermuten, dass die regulären Kurven unter den kompakten Kontinua neben den oben angeführten Kennzeichnungen auch durch ihre Eigenschaft charakterisiert sind, nebst allen ihren Teilkontinua zusammenhängend im kleinen zu sein.

8. *Die gewöhnlichen Kurven.* Zunächst ergibt sich, dass die einfachen Kurvenbögen unter den kompakten Kontinua dadurch charakterisiert sind, dass sie die einzigen sind, welche abgesehen von zwei Endpunkten ausschliesslich Punkte zweiter Ordnung oder, wie wir sagen wollen, gewöhnliche Punkte enthalten. Jene Kontinua nun, die abgesehen von höchstens endlich vielen End- und Verzweigungspunkten ausschliesslich gewöhnliche Punkte enthalten, nennen wir gewöhnliche Kurven. Zum Punkt  $p$  von der Ordnung  $n$  einer gewöhnlichen Kurve  $K$  existieren genau  $n$  einfache Teilbögen von  $K$ , welche bloss den Punkt  $p$  gemein haben. Die gewöhnlichen Kurven sind, wie sich daraus leicht ergibt, identisch mit den Summen von endlich vielen einfachen Kurvenbögen, die höchstens die Endpunkte miteinander gemein haben. Ist  $p$  von der Ordnung  $n$ , dann hat die Begrenzung jeder hinlänglich kleinen zusammenhängenden Umgebung von  $p$  die Mächtigkeit  $n$ . Sind die ganzen, nicht negativen Zahlen  $\alpha_1, \alpha_3, \alpha_4 \dots \alpha_n$  vorgegeben, so ist notwendig und hinreichend für die Existenz einer beschränkten gewöhnlichen Kurve, welche ausser  $\alpha_k$  Punkten der Ordnung  $k$  ( $k = 1, 3, 4 \dots n$ ) bloss gewöhnliche Punkte enthält, das Bestehen der Relationen:

$$\sum_{k=1}^n k\alpha_k = 0 \quad (2)$$

$$\alpha_1 \equiv \sum_{k=3}^n k\alpha_k - 2 \left( \sum_{k=3}^n \alpha_k - 1 \right).$$

Durch diese Sätze wird der *Anschluss an die kombinatorische Topologie* der eindimensionalen Mannigfaltigkeiten hergestellt.

Es sei zum Abschluss bemerkt, dass wir dieser auf eine Dimensionstheorie gegründeten Kurventheorie eine Lehre von den Flächen, den Körpern und den  $n$ -dimensionalen Körpern an die Seiten stellen können.

**Anatomy.** — “*The meninges in Cyclostomes, Selachians, and Teleosts, compared with those in man.*” By Dr. C. U. ARIËNS KAPPERS.

(Communicated at the meeting of November 29, 1924.)

The meninges in lower vertebrates are very different from those in mammals and man.

Though formerly — misled by superficial resemblances — also in Cyclostomes and Plagiostomes, a dura mater, arachnoidea and pia were supposed to exist, at the present time this supposition is only maintained in the “*Mikroskopische Anatomie der Wirbeltiere (Heft IV)*”, published in 1923, by R. KRAUSE, who however does not seem to have studied this subject very accurately.

Already in 1884 SAGEMEHL (l. c.) pointed out that a real arachnoidea does not occur in fishes, and that the widelymeshed tissue formerly considered as such, really lies between the so-called internal and external (periostal) dural membrane, and STERZI<sup>1)</sup> (l. c. 1900—1901) in his comparative anatomy of the meninges emphasized that in Cyclostomes and Plagiostomes only one undifferentiated meninx is found, which he called *meninx primitiva*, and considered to be the origin of the dura, arachnoidea and pia in higher animals.

My own researches confirm STERZI's opinion regarding Cyclostomes and Selachians. It has however to be emphasized that only the internal dural membrane develops from the *meninx primitiva*, the external or periostal dural membrane originating from the endostal (or endochondral) connective tissue that generally in lower vertebrates lies at a great distance from the *meninx primitiva*, and consequently far from the origin of the internal membrane. In my opinion it is better (c. f. also GEGENBAUR<sup>2)</sup>, POIRIER and CHARPY<sup>3)</sup>, TESTUT<sup>4)</sup>, STERZI<sup>5)</sup> and RAUBER<sup>6)</sup>) not to

1) STERZI. Ricerche intorno all' anatomica comparata ed all' ontogenesi delle meningi. Atti del reale istituto veneto di scienze, lettere ed arti. Anno accademico 1900—01. Tomo 60. Parte II.

See also: STERZI. Recherches sur l'anatomie comparée et l'ontogénèse des meninges. Archives italiennes de biologie, Tomo 37, 1902.

2) GEGENBAUR. (Lehrbuch der Anatomie des Menschen, 6te Auflage 1896, Bnd. II, Page 441) speaks of the „von der inneren Lamelle gebildete eigentliche Duralsack des Rückenmarkes“.

3) POIRIER et CHARPY. Traité d'anatomie humaine, Tome III, 1er fasc. Paris, 1901, p. 107.

4) TESTUT speaks of the internal membrane as „dure mère proprement dite“. See: Traité d'anatomie humaine, 6ième Edition, Paris 1911, p. 1050—1061.

5) STERZI. Intorno alla divisione della dura madre dell' endocranio. Monitore zoologico italiano, Anno XIII, 1902.

6) Also RAUBER in his Lehrbuch der Anatomie des Menschen (1e Auflage 1903, Bnd. II,

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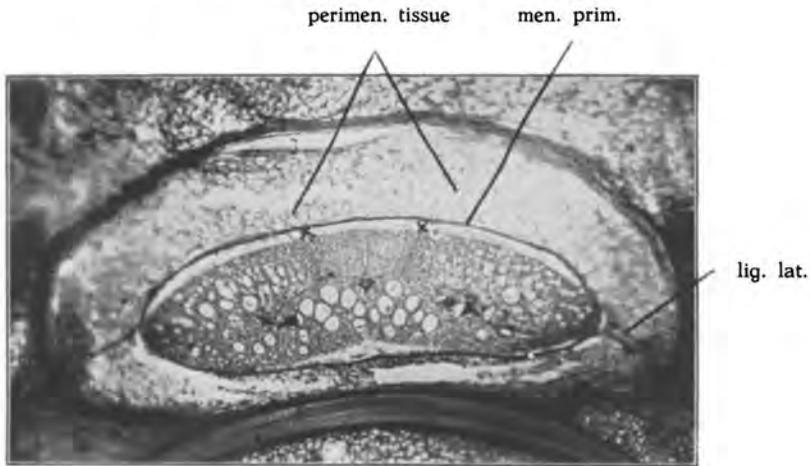


Fig. 1. Spinal cord of Petromyzon in situ  
x x Space between meninx primitiva and cord, caused by retraction.

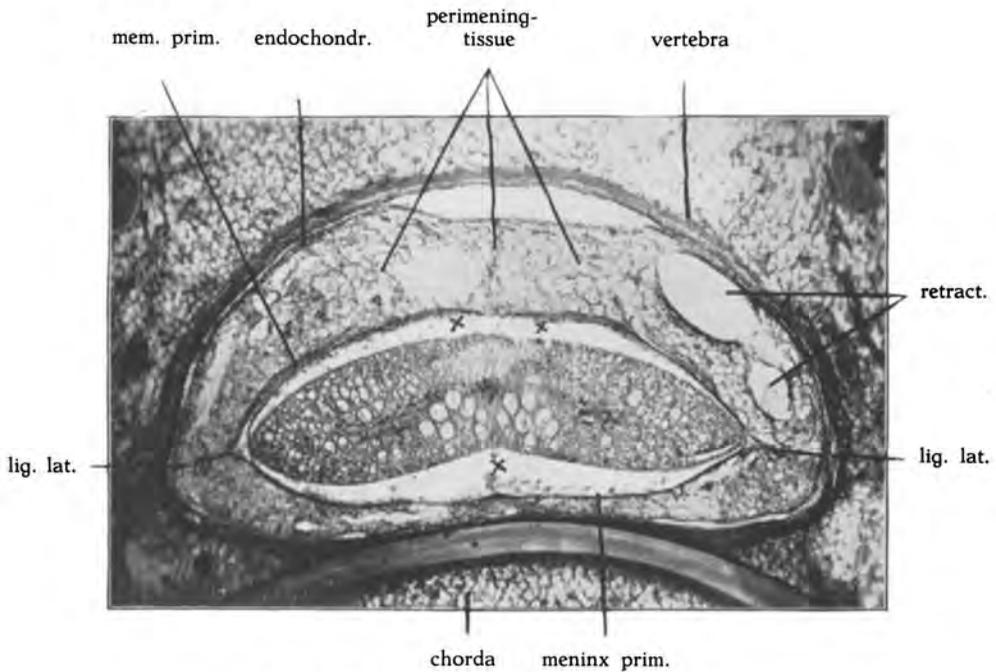


Fig. 2. Spinal cord of Petromyzon in situ.  
x x x Spaces caused by retraction.

consider the so-called external or periosteal membrane of the (spinal) dura (which follows all the sinuosities of the bone) as a part of the dura proper, though it fuses with it in the cranial cavity in the adult (after an embryonic condition in which it may be distinguished from it).

The distinction of a periosteal and an internal layer in the *dura mater spinalis* only leads to confusion and to the idea of an ambiguous membrane, which ambiguity disappears by leaving the so-called periosteal dural membrane there, where it belongs after its nature and origin, viz. to the connective tissue of the endochondrium or endost and not to the dura.

Concerning the Cyclostomes, I found in *Petromyzon fluv.* (fig. 1 and 2) relations, as described by STERZI.

The *medulla spinalis* is surrounded by a single membrane in which no differentiation into separate layers is visible. I call this membrane, with STERZI, *meninx primitiva*. It is continuous with the sheath of the roots.

This membrane, which shows strong lateral ligaments extending far laterally into the perimeningeal tissue (fig. 1, 2) does not yet penetrate with septa into the substance of the spinal cord, so that the membrane easily detaches (XX) from the cord. The nutrition of the spinal cord has to pass everywhere through the superficial glious layer (*limitans superficialis*)<sup>1)</sup>, there being no intramedullary septa and intramedullary vessels.

Outside this *meninx primitiva*, which, as I shall show later on, also contains the anlage of the *dura mater* (in the sense of the word mentioned above) lies a broad layer of large cells, which is to be considered as a filling-tissue and reaches as far as the endochondrium of the vertebrae.

This perimeningeal tissue consists of round and oval mucous cells.

In some of my preparations spaces occur, that look like epidural sinusses, which also in human embryos (v. GELDEREN l.c.) are found between the so-called interior layer of the dura and the so-called periosteal layer. I could not find however traces of blood here. They are also more or less local spaces that do not spread over a great length. As I could not find any connection with the *venae invertebrales*, they probably are retraction cavities (caused by the fixation).

The relations in Plagiostomes do not show much difference herewith.

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p. 337) speaks of "*Lamina interna oder Dura spinalis in engerem Sinne*". A similar opinion is given in CUNNINGHAM's *Textbook of Anatomy* (3d Ed. 1909, page 600).

<sup>1)</sup> Already in Selachians, meningeal septa with bloodvessels grow into the spinal cord, causing a closer relation between the nervous substance and the vascular system. As however the *limitans gliosa superficialis* grows at the same time with those septa, a real penetration of meningeal tissue into the nervous substance itself does not occur. In fact the septal spaces are to be considered as the fissures in the forebrain, with this difference that they are much smaller and for the greater part filled up with pia tissue, while the arachnoidal cavities in the brain fissures are much wider and go further downwards. They also resemble each other by the fact that the *dura* remains outside them, in the brain, as well as in the spinal cord.

In *Scyllium* I also found only one meninx, to be called *meninx primitiva*, in which no differentiation in separate layers is visible. It contains small blood vessels, that penetrate with meningeal septa into the spinal cord.

Moreover the sharks show the four spinal ligaments already described by STERZI: the rather strongly pronounced lateral ligaments (fig. 3 and 4), and the thinner, often scarcely developed, dorsal and ventral ligament. Only the lateral ligament extends for some distance through the perimeningeal tissue. The others are merely thickenings of the *meninx primitiva*. Besides this *meninx primitiva* which just as in Cyclostomes, continues in the rootsheath, a large amount of peri-meningeal tissue is found which reaches as far as the endochondrium and shows much more widely spread meshes than in Cyclostomes.

Only here and there — especially in the neighbourhood of the endochondrium — it is a little more compact (fig. 4).

Large thinwalled veins (without muscular coat) are seen in the perimeningeal tissue, especially on the dorsal and lateral side. There is no doubt as far as concerns their homology with the so-called epidural veins in mammals and man, though they are relatively much larger and therefore resemble sinusses.<sup>1)</sup>

The relations in Ganoids (*Acipenser* and *Polyodon*) are similar to those in Selachians: so I shall not describe them again.

My researches concerning the relations in the most specialized group of fishes, the *Teleosts*, show that there are in this subdivision large differences in meningeal structure that *might* explain the rather different descriptions present in literature, if the chief and rather different descriptions — those of SAGEMEHL and STERZI — were not both based partly on the same material.

STERZI (l.c. I, page 1142) examined especially *Tinca* and further *Cyprinus*, *Esox*, *Barbus*, *Muraena*, *Anguilla*, *Rhombus*, *Solea* and *Labrax*, and found everywhere under the generally perimeningeal tissue only one meninx, which he calls *meninx primitiva*, just as in Cyclostomes and Plagiostomes.

He distinguishes therein two layers, an exterior and interior layer. The *exterior layer* is very thin and consists almost entirely of large flattened cells, more or less pigmented. Further there are star-shaped cells and some cells with long offshoots and connecting ramifications. Between them there are some pigmentcells. In this layer also some elastic fibres are seen. He does not speak of a fibrous thickening of this exterior layer which might indicate a dural development.

The interior layer is more developed. On this<sup>2)</sup> (in this?) layer, the bloodvessels occur that supply the medulla. It consists of connective tissue fibrils and elastic fibres, crossing each other in different directions.

He further mentions the ligaments and remarks that the sheath of the meninx continues in the rootsheath.

Concerning the perimeningeal space, he remarks that the latter is well developed dorsally

<sup>1)</sup> Similar large epidural veins occur in Carnivora, Edentates, Cetacea and Elephas, where the epidural space still prevails on the arachnoidea.

<sup>2)</sup> The author (l.c. page 1143) says: "Su di esso poggiano i vasi."

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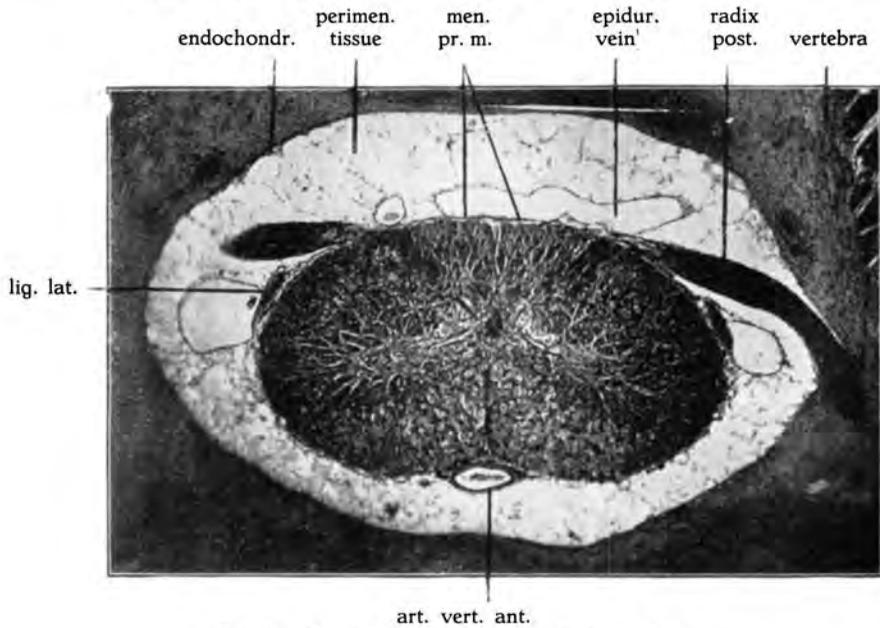


Fig. 3. Spinal cord of *Scyllium canicula* in situ.

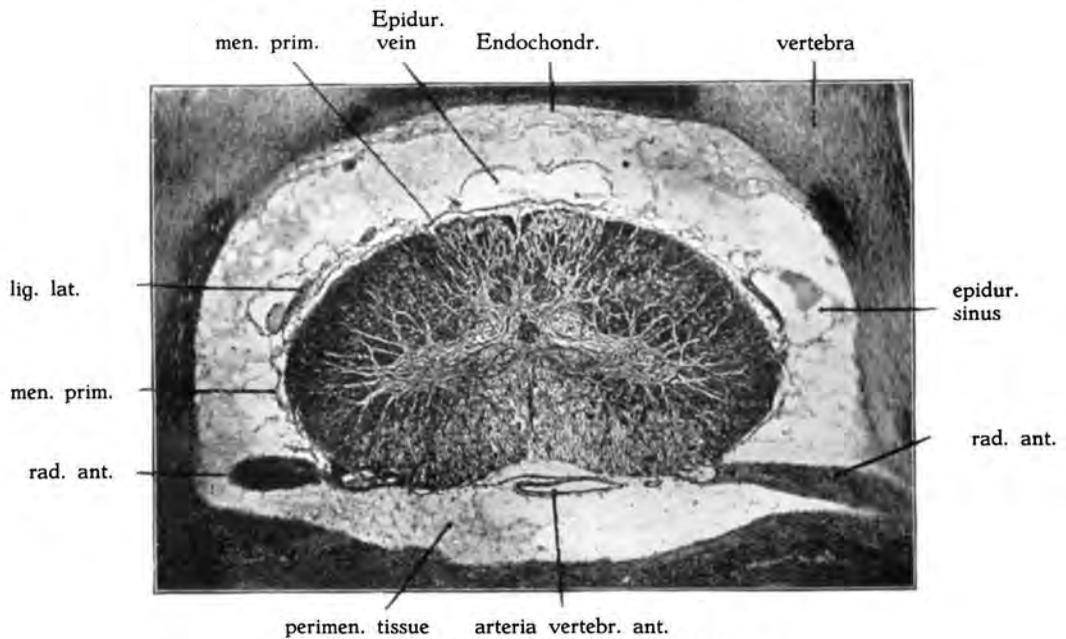


Fig. 4. Spinal cord of *Scyllium canicula* in situ.

and ventrally but may be reduced laterally to a narrow fissure. The perimeningeal tissue <sup>1)</sup> in this cavity consists of fine trabecles between which lie large fatcells. Also many small vessels are found there. It has the function of a perimeningeal filling-tissue. Similar relations were found in the other bony-fishes which he examined.

Quite different was the description given before him (1884) by SAGEMEHL<sup>2)</sup> who in *Siluroides* and *Cyprinoidea* (especially in *Barbus* and *Perca*) distinguishes two meninges, distinctly separated by a fissure, which he calls "pericerebraler Lymphraum" and which he considers to be the homologue of the subdural fissure in mammals.

The membrane lying interiorly to this fissure is, according to him, the origin of both the pia and arachnoidea<sup>3)</sup>, although one cannot yet distinguish therein those two membranes. The only distinction to be made in this "vascular-membrane" ("Gefäßhaut" as he calls it) is that only the interior layer of this membrane continues into the fissure *mediana anterior*, while the exterior layer lies over it like a bridge. Thus far his description of the part lying under the subdural fissure.

Everything outside the "pericerebraler Lymphraum"<sup>4)</sup> SAGEMEHL considers as a *dura mater* in the old sense of the word, considering as such not only our fibrous dural membrane, but also our perimeningeal tissue and our periosteal membrane (l.c. page 460—464).

Resuming we may say that there is a good deal of difference between the opinions of SAGEMEHL and STERZI. STERZI presumes that in fishes there is only one meninx which he calls *meninx primitiva*, which includes both the *dura* and the *lepto-meninges* in an undifferentiated state, while SAGEMEHL distinguishes a dural membrane and under it, separated by a fissure, a tissue which is the origin of pia and arachnoidea (a *meninx secundaria* as STERZI calls it in Reptiles and Birds). This *meninx secundaria* ("Gefäßhaut" of SAGEMEHL) shows only in some places a differentiation in an inner and outer membrane, which however has nothing in common with the differentiation in arachnoidea and pia.

The difference between these authors is the more striking as both, at least partly, examined the same material (*Barbus*).

Personal researches convinced me that the relations in Teleosts may be very different. I examined a very small Teleost, *Girardinus*, and compared it with a fish which may attain a very considerable size, *Lophius piscatorius*, and found very different relations.

In *Girardinus* no differentiation is visible in the meningeal tissue sur-

<sup>1)</sup> He (and also SAGEMEHL) remarks that the perimeningeal tissue is mucous in Elasmobranchs and Ganoids, and adipose in Teleosts (l.c. page 1147). This is not always correct according to my experience. An *Acipenser sturio* in my collection has for instance a large quantity of perimeningeal fat tissue, and I found mucous tissue in several Teleosts. It seems that both these tissues are most fit to serve as an buffer substance in a movable enclosure.

<sup>2)</sup> SAGEMEHL. Beiträge zur vergleichenden Anatomie der Fische II. Einige Bemerkungen über die Hirnhäute der Knochenfische. Morphologisches Jahrbuch Bnd. IX, page 457, 1884.

<sup>3)</sup> For the Teleosts KRAUSE's description is practically in accordance with SAGEMEHL. He, however, does not mention SAGEMEHL's name and considers the interior layer entirely as a *pia mater*, (l.c. page 647). That the interior layer contains the origin of both pia and arachnoidea, is not mentioned by KRAUSE.

<sup>4)</sup> This word has nothing to do with the so-called epicerebral space of HIS, which this author abusively supposed to exist between *membrana limitans gliae* and the *intima piae*.

rounding the spinal cord (and the brain). So here with STERZI one may really speak of one *meninx primitiva* which also joins the periost, at least laterally where hardly any perimeningeal space is seen between vertebra and *meninx* (fig. 5).

Dorsally, where the space between the *meninx* and periost is wider, there occurs in this space a very thin, exceptionally widelymeshed perimeningeal tissue, in which, especially at its dorsal side, large veins appear. The same is found in the area of the oblongata and cranium, with this difference however, that there is a much larger quantity of perimeningeal tissue in the much larger cranial cavity. But neither here a differentiation is visible in the *meninx primitiva*. Consequently, with regard to this animal, STERZI's description is correct.

In *Lophius piscatorius* quite other relations were found. Here also a large quantity of widely meshed peri-meningeal tissue. The actual meningeal tissue lying under it however shows a vere distinct differentiation, in two membranes (fig. 7 and 8).

The outer part of the tissue lying under the widely meshed perimeningeal mucous tissue forms a dense fibrous layer which in some places is larger than in others, but which may be seen everywhere as a distinct layer. If this layer were separated from the underlying meningeal tissue by a continuous split, one would be right in speaking of a well differentiated *dura mater*. Such a *continuous* split as described by SAGEMEHL and called "pericerebraler Lymphraum" analogous to the subdural cavity in mammals, I cannot find in *Lophius*. The relations here are similar to those observed by VAN GELDEREN<sup>1)</sup> in early human embryos. This author found that the (interior layer of the) ectomeninx has become a denser tissue already in human embryos of 19.6 mm. (l.c. I page 2850), contrasting distinctly with the leptomeningeal tissue lying under it without being however separated from it by a fissure, which he even did not yet find in a stage of 25—30 mm., but only saw, occurring first as local dehiscences, in an embryo of 35—40 mm.

The same condition I found in *Lophius*, where I could not perceive a continuous split, but only local dehiscences between the dural membrane and the tissue of the *meninx secundaria* lying under it. (see fig. 8).

Yet I do not hesitate to consider the fibrous exterior membrane of the *meninx primitiva* in *Lophius* as dural tissue, as the fibrous condensation proves that it is developing into the direction of the strongly fibrous *dura mater* and not into the direction of the arachnoidea, which is becoming much more widelymeshed. If there were a continuous fissure, then it would not be correct to speak of an exterior dural membrane of the

<sup>1)</sup> V. GELDEREN. De ontwikkeling der sinus durae matris bij den mensch.

Ned. Tijdsch. v. Geneeskunde, Vol. 68, 1924, Iste Helft, N<sup>o</sup>. 25, Pag. 2850, and Vol. 58 of the Anatom. Anzeiger, 1924. "Zur vergleichenden Anatomie der Sinus durae matris".

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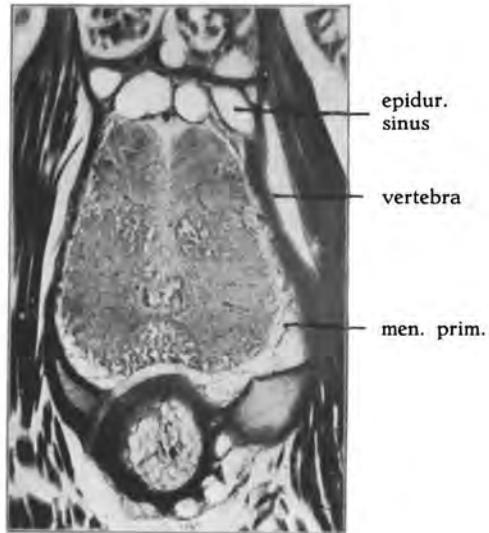


Fig. 5. Spinal cord of *Girardinus* (cervical).  
In situ.

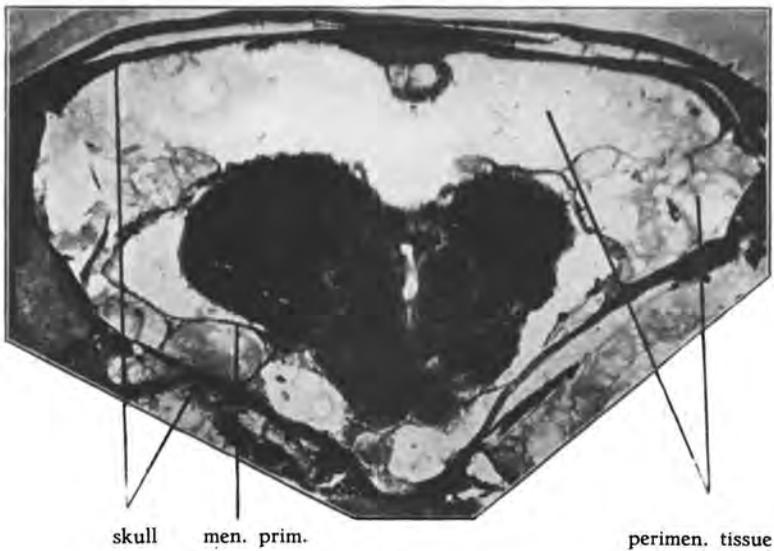
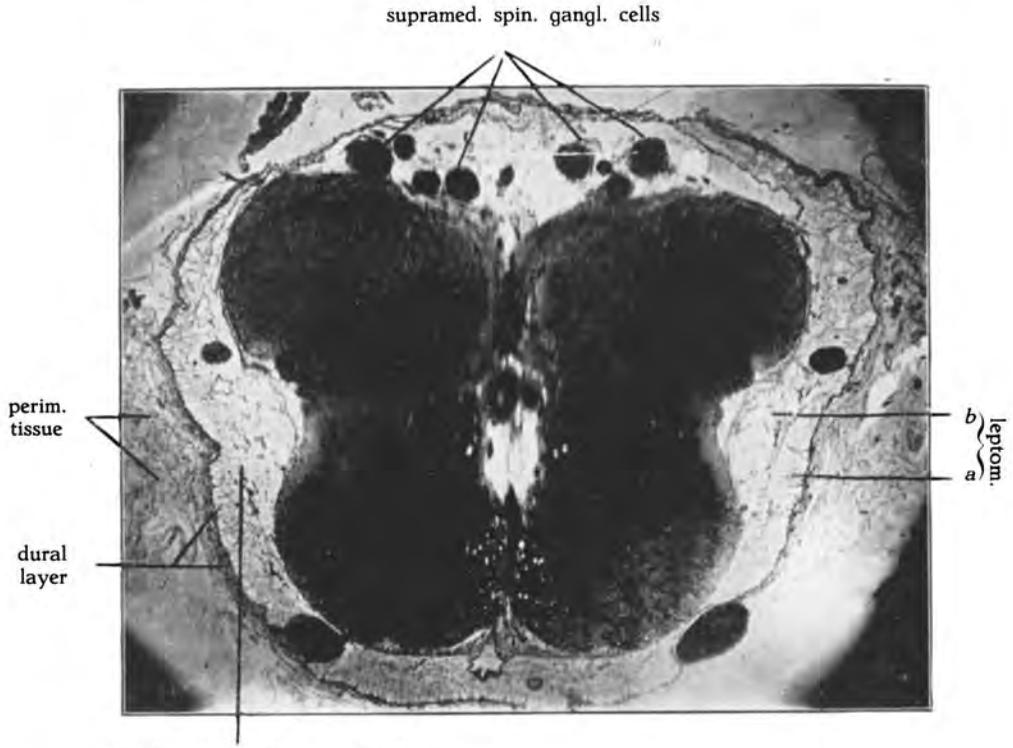


Fig. 6. Frontal part of the midbrain of *Girardinus* in the skull.

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leptomeninx (men. secundaria)

Fig. 7. Cervical cord of *Lophius* in the meninges.

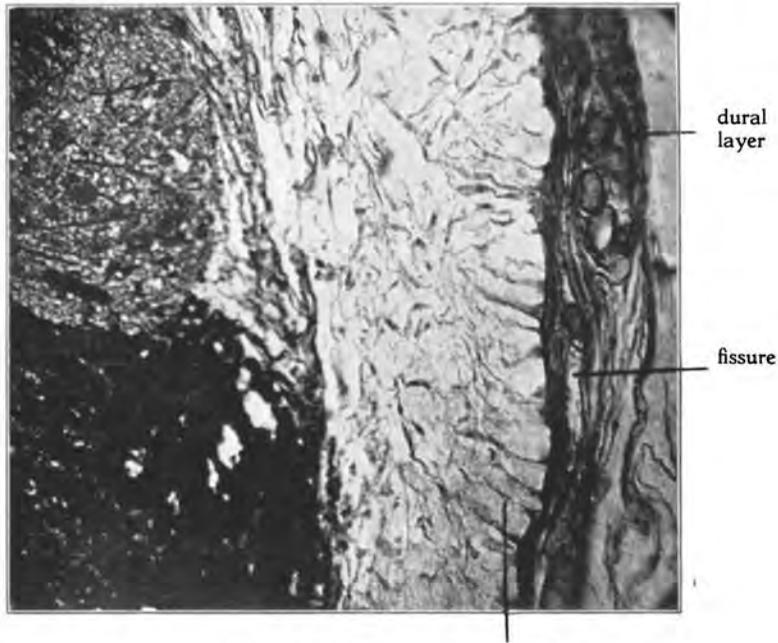


Fig. 8. Enlarged photograph of the meninges in *Lophius*.

meninx primitiva, but of a real dura mater and a meninx secundaria, as they occur in Reptiles.

Concerning the condition of the inner layer of the meninx, its much more widely meshed character is striking (fig. 8—10). In many places we may distinguish in it an exterior layer *a* from an interior layer *b* (see fig. 7—9). In the former, lying directly underneath the mesothelial layer by which it is covered, the cells often stand almost perpendicularly (like palisades) on the external layer of flat cells (fig. 8 : *a*), while the meshes of the interior part are much less regular. Another difference is that only the interior layer follows the fissures and the septa and moreover it contains more small bloodvessels, running in that part that lies immediately on the limitans gliae.

Though there is here a fairly widely meshed tissue, especially in the palisade-part, according to my opinion we may not compare this with the trabecular tissue of the arachnoidea since real "trabecles", that is to say fibrillar threads of connective tissue covered with mesothelial cells, do not occur here. The pseudo-trabecles are ramifications of single cells and consequently might be called *monocellular trabecles* similarly as those occurring in the widely meshed reticular tissue of lymph glands. Moreover in real arachnoid tissue the meshes are much wider and the trabecles far less numerous.

Another argument pleads for this. In mammals the arachnoidea has very wide spaces just at the dorsal side of the oblongata on the choroid of the fourth ventricle (cisterna posterior cerebelli) and communicating with the ventricle by means of the foramen Magendi (where this occurs). In *Lophius*, however, the widely meshed leptomeningeal tissue surrounding the whole surface area of the spinal cord (fig. 7) on all sides, in the area of the calamus (fig. 9) is dorsally a little less developed, and on the choroid roof still less so, being especially developed at the lateral and ventral sides of the oblongata<sup>1)</sup> (see fig. 10).

This seems to be in favor of my opinion that this tissue does not yet perform an important function as a receptaculum of ventricular fluid, running into it in higher animals and forming most of the liquor cerebrospinalis externus, but here performs chiefly the same function as widely meshed reticular connective tissue does in other places, f. i. in the intestina and lymph glands.

That this differentiation occurred in *Lophius* and not in *Girardinus* may perhaps be partly due to the much larger space of the vertebral canal in the latter. In larger fishes the skull and vertebral canal increase much more than the nervous system itself, and owing to that the tissue lying between them also increases considerably. That this increase which is very obvious in the perimeningeal tissue in *Lophius*, does not only

<sup>1)</sup> Ontogenetically WEED (Anat. Rec. Vol. 10, 1916, p. 479) found the meningeal differentiation also occurring first in the basal parts.

concern the perimeningeal tissue (as happens in the cranial cavity of *Girardinus*, which also is much larger than the vertebral canal of this animal, fig. 6) but in *Lophius* also holds good for the meningeal tissue itself, points however to a higher differentiation<sup>1)</sup> to a stage immediately preceding an arachnoidal development.

Thusfar the results of my microscopic research on the meninges in fishes, where the large quantity of perimeningeal, mucous or adipose tissue stands prominent: its quality of a buffer tissue being of great use to the large flexibility of fishes<sup>2)</sup>. We know that traces of a thin perimeningeal adipose tissue still occur in man, in the space between the actual dural membrane and the endost of the vertebrae, while it disappears in the cranial cavity, which is much less subject to changes in form<sup>3)</sup>.

The comparison of the relations between fishes and man, however, asks for a further explanation as far as concerns the development of the arachnoidal spaces and the liquor cerebro-spinalis externus.

There is no doubt that the lowest vertebrates as Cyclostomes, Plagiostomes and Ganoids do not have actual arachnoidal cavities and consequently no liquor cerebro-spinalis externus which in mammals fills the subarachnoidal cavities and whose total volume in man considerably surpasses the volume of the liquor cerebro-spinalis internus (ventricular fluid).

Together with the want of liquor cerebro-spinalis externus, we see the striking fact that the liquor cerebro-spinalis internus — the ventricular liquor — is not seldom very richly developed in lower fishes.

This relative large volume of liquor cerebro-spinalis internus, is not only proved by the wide ventricles in Plagiostomes (especially sharks) and Cyclostomes, but also by the fact that, where these ventricles are covered at the surface by a choroidal membrane, this membrane generally bulges outward considerably, as is shown e.g. in the fourth ventricle and the roof of the midbrain of *Petromyzon* (fig. 11). Also other primitive fishes — f. i. *Ceratodus* (v. D. HORST) — have similar protruding choroid membranes, and with some fishes (*Lepidosteus* and *Amia*), the choroid roof of the third ventricle (the so-called parencephalon) even evaginates in such a degree to all sides that choroidal sacks are formed filled with liquor internus, extending outside alongside the brainwall, far frontally as well as caudally<sup>4)</sup> (fig. 12).

1) *Girardinus* belongs to the Haplomi, that are considered to stand at a lower level than the group of the Pediculati, to which *Lophius* belongs.

2) The fact that the flexions made by fishes in swimming are chiefly lateral may perhaps explain the preponderance in the size and development of the lateral ligaments.

3) Compare also POIRIER et CHARPY, l.c. page 107.

4) ARIËNS KAPPERS. Untersuchungen über das Gehirn der Knochganoiden, *Amia calva* und *Lepidosteus osseus*. Abhandlungen der Senckenbergischen Naturf. Gesellschaft, Frankfurt a/Main, 1907.

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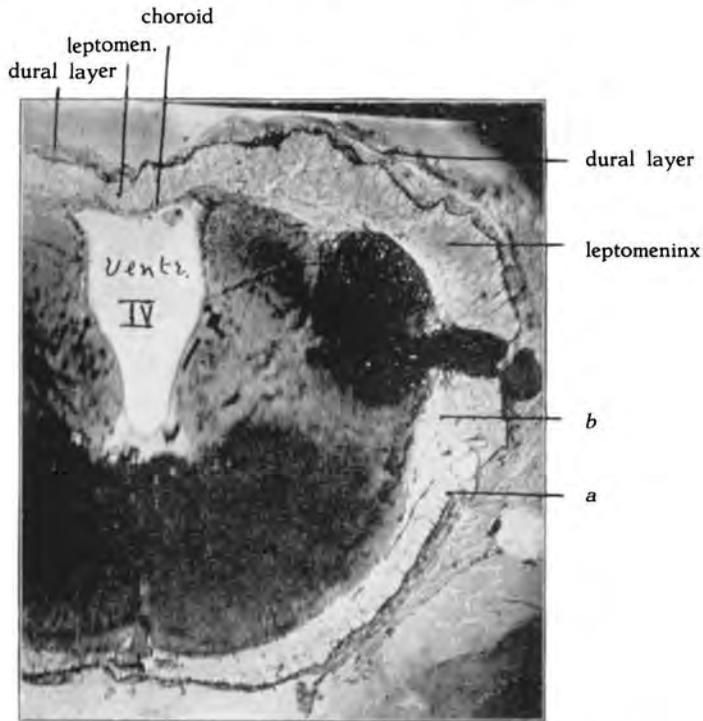


Fig. 9. Lophius. Oblongata on the level of the Calamus.

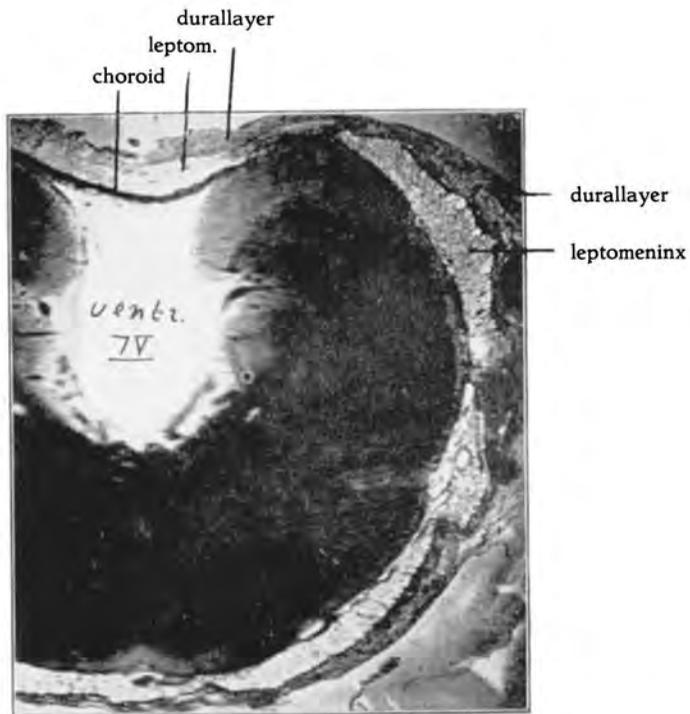


Fig. 10. Meninges of Lophius immediately behind the cerebellum.

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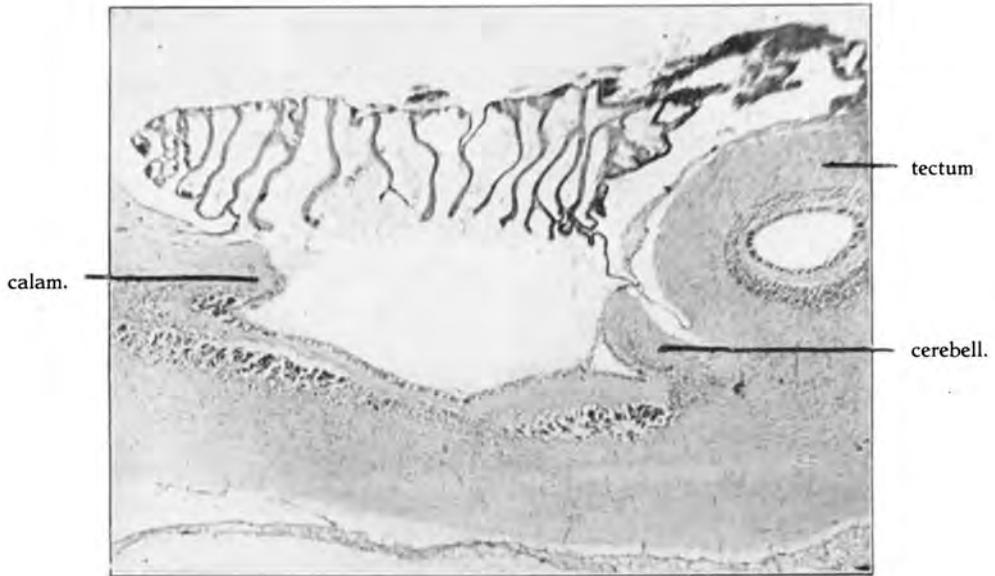


Fig. 11. Fourth ventricle with high choroidal roof in *Petromyzon fluviatilis*; sagittal.

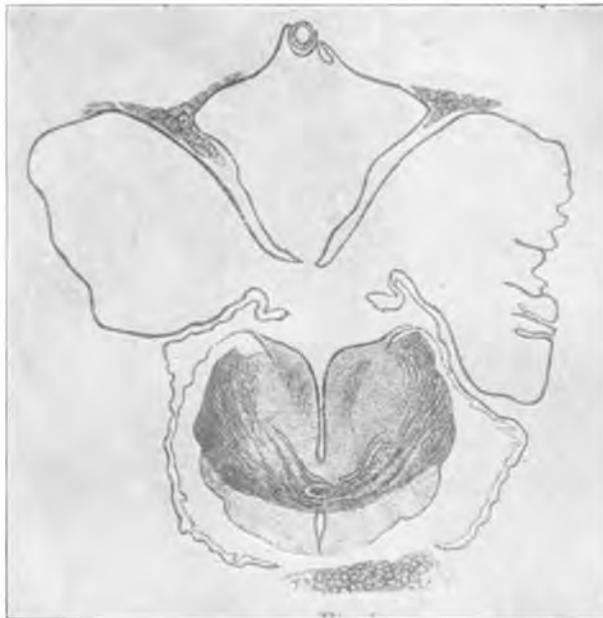


Fig. 12. Cross section through the frontal part of the thalamus with large recessus dorsalis, laterales and ventrales of the choroid of the third ventricle in *Lepidosteus osseus*.

It is evident by all this that the liquor internus has a relatively large volume in many lower animals, in strong contrast to the absence of arachnoidal cavities and liquor externus.

It is interesting that in higher animals, especially mammals — where the arachnoidal cavities with their liquor externus develop very strongly, <sup>1)</sup> and at last surpass the volume of the ventricular liquor — the choroid-membranes do no more use as sacks, but (with few exceptions) <sup>2)</sup> grow inwards into the ventricles as ventricular draining organs.

In my handbook of comparative brain-anatomy (part II, page 820) I already stated that the coincidence of the accumulation arachnoidal liquor on one hand, and the growing of the choroid membranes into the ventricles on the other (secreting liquor into and at the same time draining the ventricles) is not accidental. It is sure that most of the liquor externus does not originate at the place where it later occurs, but — certainly for the greater part — originates from the ventricular fluid, which diffuses through the choroid-membranes (with or — in most mammals — without assistance of foramina of LUSCHKA or MAGENDI <sup>3)</sup>).

This origin of liquor externus certainly is the most important one, though it may be added that in some places a slight diffusion of ventricular liquor takes place through the ependyma of the ventricles, and arrives into the Virchow-Robin spaces round the brain-vessels and so in the arachnoidal cavities.

In connection with this it is interesting that Dr. FREDERIKSE in the Institute for Brain-research could prove the existence of so-called „Kittsubstanz“ (as also occurs between choroid cells and between intestinal epithelium) between the ependyma cells of the ventricles in the lizard.

In view of the fact that the liquor arachnoidalis originates certainly for the larger part by the diffusion of ventricular fluid through the choroid, it is not strange that the formation of the arachnoidal sacks in mammals arises at the same time with a more draining action and inversion of the choroid.

Of both choroidal functions, viz. the secretion of liquor into the ventricle <sup>4)</sup> at one side, and at the other the draining of ventricular fluid,

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<sup>1)</sup> Smaller arachnoidal cavities occur already in birds, as HANSEN PRUSS could show by injections. Journ. of Comp. Neur. Vol. 36, 1923.

<sup>2)</sup> The recessus laterales of the oblongata.

<sup>3)</sup> These foramina are seen for the first time in mammals and do not occur in all mammals. They are even sometimes (but rarely) failing in man.

<sup>4)</sup> The ependyma also takes some part here in, at least in some places (f.i. the infundibulum, see my book, Vol. II, page 821, fig. 437, and page 853, fig. 455 A and B) and the communications of WICLOCKI and PUTNAM. Note on the anatomy of the areae postremae, Anat. Record Vol. 19, 1920 and: Further observations on the anatomy and physiology of the areae postremae; Anat. Record, Vol. 27, 1924.

the first mentioned function occurs first<sup>1)</sup>, and this explains as well the strong protrusion of the choroidal sacks in lower fishes, as the absence of proper arachnoidal cavities in these animals.

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<sup>1)</sup> That this process repeats itself in the same order in embryologic development is shown by the researches of LEWIS WEED, who proved that while the ventricular liquid appears in embryos already in the first stage of ventricular development, the liquor externus is found in the arachnoidal cavities of the pig for the first time in an embryo of 14 mM. See his researches: Development of the cerebro-spinal spaces in pig and man: Contributions to embryology, published by the Carnegie Institution, Vol. V, 1917.

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**Anatomy.** — “Some notes upon the finer anatomy of the Brain Stem and Basal Ganglia of *Elephas indicus*”. By Dr. A. PŘECECHTEL, Prague. (Communicated by C. U. ARIËNS KAPPERS).

(Communicated at the meeting of January 31, 1925).

Until now the brain of the Elephant has been studied chiefly macroscopically, especially by DEXLER<sup>1)</sup>, whilst BOLK<sup>2)</sup> gave us a minute description of the cerebellum. Concerning its fiber relations, only a description of the rhinencephalon has been given (BINDEWALD)<sup>3)</sup>.

Studying the microscopical sections of *Elephas indicus* in the Central Institute for Brainresearch in Amsterdam, I found several relations in the oblongata, midbrain, thalamus, and basal ganglia, that are of great interest and will be briefly recorded. For comparison several other animals were examined in sections, stained in the same way as the elephants brain, viz. after WEIGERT—PAL en VAN GIESON.

In the cervical cord, the relation of the grey and white matter strikes even the naked eye, the white matter being very abundant, the grey matter relatively scanty. This fact is compatible with the observations made by HOVY<sup>4)</sup>, on a whole series of mammals, proving that concomitantly with the size of the body the mutual relation of the two substances modifies in favour of the white matter.

In the *posterior horn* the *substantia gelatinosa* (fig. 1, s. g.) is well developed as it is also in the nearest relatives of the Elephant, the Ungulates. This is still more striking (fig. 2) in the upper cervical region where the strong descending Vth ends.

The *substantia gelatinosa* is arranged in folds, as is frequently the case with a greater development of receptive grey matter in the central nervous system (KAPPERS)<sup>5)</sup> and equally occurs in the spinal cord of Ungulates (BIACH<sup>6)</sup>).

1) DEXLER. Zur Anatomie des Nervensystems von *Elephas indicus*. Obersteiner's Arbeiten, 1907. Festschrift.

2) L. BOLK. Das Cerebellum der Säugetiere. Bohn, Haarlem, 1906.

3) BINDEWALD. Das Rhinencephalon von *Elephas indicus*. Zoolog. Jahrb. (Anat. und Ontog.) Bnd. 35, 1913.

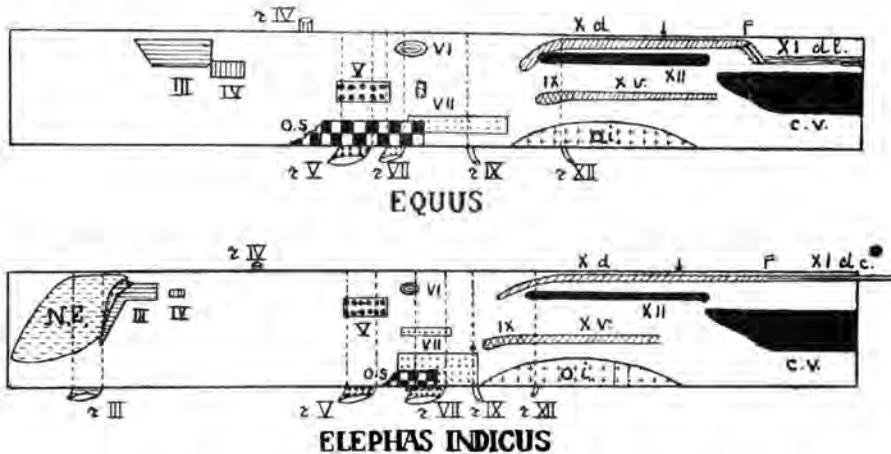
4) HOVY. On the relation between the quantity of white and grey substance in the central nervous system. These Proceedings, 16. p. 311.

5) ARIËNS KAPPERS. Ueber das Rindenproblem und die Tendenz innerer Hirnteile sich durch Oberflächenvermehrung statt Volumzunahme zu vergrößern. Folia Neurobiologica, Bnd. VIII, No. 4, 1914.

6) BIACH. Das Rückenmark der Ungulaten. Obersteiner's Arb. Bnd. 16, 1908.

The two posterior funiculi distinctly differ from one another by the thickness of their fibres. The neurones of the medial fascicle (GOLL) are thicker than those of the lateral fascicle (BURDACH). This may be explained by the fact that the medial posterior funicular bundle is longer than the lateral posterior bundle, since JOHNSTON<sup>1)</sup> has pointed out that an axon often increases in a cellulo-fugal direction.

Dorsally to the *frontal horns* of the cervical region the *nucleus accessorii* is found lying medially in the central zone between the anterior and posterior horns, its root fibres running laterally in a dorsally concave arch (see fig. 2) and leaving the cord between the anterior and posterior root, but nearer the posterior root.



Diagrams showing the difference in topography of the motor nuclei in the horse (VERMEULEN) and Elephant. The arrow indicates the calamus, the flag the hindpole of the dorsal X nucl.

The cells of the nucleus accessorii are polygonal, and form a dorsal column that is not characterized by an invariably equal thickness, but arranged like a string of beads, reaching much further caudal into the cervical medulla than in any other mammal. In cranial direction this nucleus XI passes almost imperceptibly into the column of cells forming the dorsal nucleus vagi. This long caudal extension of the nucleus accessorii in such a dorso-central position is very rare in mammals. Mostly this part of the accessorius nucleus shows a more lateral location, although these lateral cells — as was demonstrated by VERMEULEN<sup>2)</sup>

<sup>1)</sup> JOHNSTON. Additional notes on the cranial nervecomponents of *Petromyzon*. *Journ. of Comp. Neurology*, Vol. 18, 1908. and "The significance of the caliber of the parts of the neurone, *ibidem*.

<sup>2)</sup> VERMEULEN. The vagus area in *Camelidae*. *These Proceedings* 17, p. 1119. and *Die Accessoriusfrage*, *Psychiatrische en Neurologische Bladen*, 1918.

and KAPPERS<sup>1)</sup> may show connections with the central or dorsal vagus group. — According to my opinion this dorso-central XI nucleus innervates the *R. internus* XI that joins the vagus peripherally and is sympathetic in function.

I suppose that it is this same nucleus that in Ungulates keeps its attachment with the dorsal X nucleus but for the main shifts more laterally in the intermediary zone. We know from the researches of BOK<sup>2)</sup> and POLJAK<sup>3)</sup>, that also in the spinal cord a more central and more lateral sympathetic group exists (which are closely related) in the intermediary zone.

I have not been able to trace the homologue of the ventro-lateral XI nucleus innervating the homologues of the sterno-cleido-mastoideus and trapezius in the sections that were available, although its existence is doubtless on account of the muscles and the big size of the spinal XI root.

At the point of transition of the cervical medulla into the medulla oblongata dorsally to the *canalis centralis*, the *commissura infima* appears, containing o. a. decussating fibres of the *fasciculus solitarius* that terminate on the contra-lateral side in the *commissural nucleus* of CAJAL, which is very conspicuous in this animal.

About the same level, the nuclei of the posterior funiculi are seen, first the more caudally situated nucleus of the funiculus of GOLL and more frontally the nucleus of the funiculus of BURDACH, the grey matter of which shows a characteristic lamellar arrangement especially in its caudal part.

The decussation of the spinal pyramids is small, its bundles bending dorsally and running caudally in the *dorsal* fascicles which is the most primitive course of the dorso-lateral pyramids and also found in some Ungulates and Marsupials.

Very striking in the elephant are the strong *fibrae acuatae externae* (f.a.c. fig. 3) running from the nuclei of GOLL, BURDACH and MONAKOW into the region of the inferior olive (*fibrae praetrigeminales*). KAPPERS supposes them to be connected with the inferior olive either directly or by collaterals. He found them strongly developed in Edentates, Anthropoids and man (l. c. p. 214, 215, 598). They run from dorso-caudal into a fronto-ventral direction (unlike the olivo-cerebellar tract).

Of the motor oblongata nuclei the facial nucleus (fig. 5) deserves mentioning on account of the close accumulataion of its cells and its distinct division in groups, a

1) ARIËNS KAPPERS. *Vergleichende Anatomie des Nervensystems der Wirbeltiere und des Menschen*, Teil I, 1920.

2) BOK. *Die Entwicklung von Reflexen und Reflexbahnen III. Die Ontogenese des Rückenmarkreflexapparates mit den zentralen Verhältnissen des N. sympathicus*. Psych. en Neurol. Bladen 1922.

3) POLJAK. *Ueber die Intermediärzone im Rückenmark der Säuger und ihr Verhältnis zum vegetativen Nervensystem*. Liječnički Vjesnik (Zagreb, 1924).

phenomenon which probably is connected with the fact that this nucleus innervates the fine stereopractic organ of this animal, the proboscis, whose sensory innervation is largely the trigeminus against whose descending tract the nucleus is located, being bordered on the medial side by the superior olive which may elaborate auditory reflexes on the external and internal ear muscles (*M. Stapedius*). A dorsal facial nucleus lies above the frontal half of the main nucleus. The VII nucleus receives many pyramidal fibres.

The arrangement of the XII nucleus resembles closely the one described by STUURMAN<sup>1)</sup> in the mouse. The nuclei of Roller are very distinct. (fig. 5). The vagus nuclei are well developed, specially the dorsal nucleus, as is generally the case with herbivora, and probably has to be explained by the large stomach of these animals (VERMEULEN l.c.).

Apart from a (rather small) abducens nucleus there seems to be an accessory VI nucl. as described by TERNI<sup>2)</sup> in rodents, lying near the descending V<sup>th</sup> tract.

The motor V<sup>th</sup> nucleus is relatively small as usually in herbivora, the largest motor V nucleus occurring in carnivora, whose jaw musculature is much more developed (KAPPERS l.c.).

*The system of the Nervus VIII and the cerebellar connections show many primitive peculiarities.*

The *nucleus ventralis nervi octavi*, situated ventrolaterally to the corpus restiforme, is not very large and has not shifted as far ventrally as f. i. in Chiroptera and in Carnivora, where the cochlear root is relatively much thicker.

Dorso-medially from the corpus restiforme there even is a cluster of oval cells of the same shape and size as the nucleus ventralis, and which may form a part of the ventral nucleus that — as in *Didelphys* (STOKES<sup>3)</sup>) — has remained in its original position.

Also the *tuberculum acusticum* is little developed and the same may be said of the *oliva superior* (fig. 6, o. s.) nearly entirely situated on the level of the nucleus nervi facialis, medially to it.

Frontally the olive can be traced a little farther than the frontal pole of the nervus facialis, but it gradually disappears in the reticular substance. The relatively small dimensions of the oliva superior are striking but the situation of the facial nucleus so near to it suggests that its reflectory relation with the facial muscles (of the ear) is very close.

The *system n. vestibularis*: The chief vestibular nucleus, the *nucleus of Deiters* with its characteristic large polygonal cells is very strong in the elephant and caudally passes into a large *nucleus vestibularis descendens* (fig. 4), terminating with the *nucleus of Blumenbach* or *Monakow*, which appears as a latero-anterior segment of the *nucleus of Burdach*.

From the Deitersnucleus and the descending VIII cells one plainly sees the fibres of the tractus Deiterospinalis running ventromedially.

The *nucleus triangularis*, medially to the nucleus of DEITERS, consist-

1) STUURMAN. Die Lokalisation der Zungenmuskeln im Nucl. hypoglossi. Anat. Anzeiger, Bnd. 48.

2) TERNI. Ricerche sul nervo abducente ed in special modo intorno al significato del suo nucleo accessorio d'origine. Folia Neurobiologica, Vol. XII, 1922.

3) STOKES. The acoustic complex and its relations in the brain of the opossum (*Didelphys virgiana*). American Journ. of Anatomy, Vol. 17, 1912.

ing of small cellular elements, is situated quite dorsally under the base of IV-ventricle. Its area is well marked, particularly in caudal levels (fig. 4 X) where it lies medially near the tractus vestibularis descendens and its nucleus, extending caudally a little farther than the commencement of the frontal pole of the nucl. hypoglossi. Here medially from it the tractus solitarius is seen with its grey substance (nucleus parasolitarius) laterally attaching to it.

The nucleus of BECHTEREW lies in the frontal continuation of Deiters nucleus at its typical place near the angle of the ventricle (fig. 5. nu. Bech.). This nucleus consists of cellgroups from which cellular strands run into the cerebellum in a frontal concave arch.

It is possible to trace a direct continuation of this nucleus as far as the medial cerebellar nucleus (nucleus tecti, fig. 5), from which it is obvious that evolutionally the two structures are associated, and that the grey matter of the oblongata has immigrated into the cerebellum (KAPPERS, VAN HOEVELL). To all appearance vestibular fibres ascend to the cerebellum along this strip of grey matter (as has been also described by VAN GEHUCHTEN). Almost completely — but not entirely — separated from the nucleus medialis or the nucleus tecti is the nucleus dentatus (nu. dent.), that is not connected either with the nucleus of BECHTEREW.

Dorsally the dentate nucleus is split, its upper part being situated more dorsally and medially, the other part being situated more ventrally and somewhat laterally.

Frontally the nucleus tecti (of which we know that it is chiefly connected with the anterior lobe of the cerebellum) extends farther than the n. dentatus.

The afferent *connections of the cerebellum* are extremely large, especially the brachium pontis (fig. 6) and the corpus restiforme (fig. 4). In these tracts there are deposits of grey substance that we may designate as the *nuclei brachii pontis* and *nuclei corporis restiformis*. If we trace the sections of the oblongata from the caudal segments, the corpus restiforme, containing reticularly arranged grey matter, begins to appear in the same sections as the posterior pole of the oliva inferior. Frontally the grey substance of the corpus restiforme increases, extending ventral laterally to the tractus trigemini descendens. Dorsally it extends to the nucleus of the descending VIII (see fig. 4). The most external layer of the corpus restiforme does not contain this grey matter. The more frontally, the more the grey matter increases and at the same time extends in strips as far as the ventral pole of the radix trigemini descendens, and occasionally as far as adjacent olive, viz. in those sections in which the tract from the olive inferior attains its greatest volume. More frontally imbedded grey substance diminishes again in the corpus restiforme until it is completely lost on the level of the frontal pole of the inferior olive. Here only from the nucleus DEITERS, i.e. from the frontal conti-

uation of the nucleus of the descending vestibularis, a short strip of grey matter extends between the trigeminus descendens and corpus restiforme.

In more proximal sections, strips of another grey substance appear in the *brachia pontis*, connecting the region of the nucleus DEITERS and its proximal continuation (the nucleus BECHTEREW) with the nuclei pontis. Since (as has already been stated above) the nucleus BECHTEREW is also contiguous with the strips of grey matter extending to the nucleus medialis cerebelli (n. tecti) it results from this that in the elephant there is a bridge of grey matter extending from the nucleus medialis cerebelli to the nuclei of the pons (fig. 5, 6: nu. br. pon.). The distribution of grey matter in the brachium conjunctivum pontis reaches even the most frontal segments of the pons. This appearance of grey matter testifying to the relation of the vestibular area both with the nuclei pontis in frontal and with the corpus restiforme and even with the oliva inferior in caudal direction, is not a regular phenomenon in adult mammals. It may however be well explained by the ontogenetic development of these structures. In 1907 ESSICK has described in man the so-called *corpus pontobulbare*. This is a strip of fibres accompanied by groups of cells and extending from the dorso-lateral somatosensitive static area in a ventromedial direction between the root of the acusticus and facialis, ventrally and frontally. ESSICK<sup>2)</sup>, confirming the work of HIS<sup>1)</sup>, has demonstrated in human embryos as well as in guinea-pig and rabbit embryos the genetical association of the oliva inferior (and nuclei arcuati) and the nuclei pontis with the static area of the bulb, just behind the cerebellum. The corpus ponto-bulbare of ESSICK indicates the path followed by the descending grey matter of this area to the pons. In our sections it is possible to see the relation between the nucleus DEITERS and BECHTEREW and the nuclei pontis, which may be neuro-biotactically understood by the collaboration of the pontine and vestibular apparatus in cerebellar function<sup>2)</sup>.

In the elephant however it is possible to ascertain also the connection of the area statica with the oliva inferior by the grey matter in the corpus restiforme which is exactly co-extensive with the length of the oliva inferior. Also this (fig. 4) may be explained by the embryological work done by HIS and ESSICK and confirmed by KOOY<sup>3)</sup> concerning the origin of many cells of the inferior olive from this area which again may be explained by the functional relation between these structures.

1) HIS. Ueber die Entwicklung des Riechlappens und des Riechganglions und über die des verlängerten Marks. Verhandl. der anat. Gesellschaft, Berlin, 1889.

2) ESSICK. The corpus ponto-bulbare, a hitherto not described nucleus in the human brain. Journ. of Anat. Vol. 7, 1907.

ESSICK. The development of the nuclei pontis and the nucleus arcuatus in man. Journ. of Anat., Vol. 13, 1912.

3) KOOY. The oliva inferior. Folia Neurobiologica, Bnd. 10, 1916. In this paper also an accurate description of the oliva inferior in the adult elephant is found.

In man a small island of grey matter is found constantly in the corpus réstiforme, as ascertained by HIROSE<sup>1)</sup> in 1920 (in 13 investigated cases). This nucleus in man is however very small, its long axis measuring 0.5—0.3 mm. in length. Its deposition is constant.

As the nucleus is situated on a level where the oliva inferior is most developed, its relation to the above mentioned structures is probable.

*In no adult animal these genetical alliances between the area statica on one hand and the pons and inferior olive on the other are so clear as in the elephant.*

The pons grey is very conspicuous. It is distinctly to be seen that the *fibrae frontopontinae*, situated in the *pes pedunculi* medially to the pyramid, bend down into the pons before the *fibrae temperopontinae*. They seem to end sooner<sup>2)</sup>. The *fibrae temperopontinae* extend a little further caudally before immersing into the pontine cellgroups which, by a strip of grey matter, are connected with the *substantia nigra* of the midbrain (fig. 7). On the lateral periphery of the isthmus region, two fascicles are striking: the spino-tectal tract (*tr. sp. t.*) and dorsally to it the ventral spinocerebellar tract (*tr. sp. c. v.*). More dorso-medially the large *brachia conjunctiva* are seen (comp. fig. 7: *br. conj.*).

#### *The midbrain.*

The *nucleus ruber*, is rather primitive in structure, the majority of its cells being very large magnocellular elements as far the frontal pole. The extension of the nucleus frontally to the emergence of the oculomotor nerve in the elephant is analogous to its relation in Ungulates (goat), as described by v. MONAKOW<sup>3)</sup>.

Laterally to it part of the fibres of the *brachia conjunctiva* extend farther on and can be frontally traced as far as the thalamus, although it is impossible to determine accurately to which nucleus they run. HORSLEY and CLARKE<sup>4)</sup> assume that this fascicle terminates at least partly in the lateral segment of the thalamus, which may be true also here.

The *substantia nigra* of the *pes pedunculi* is particularly developed in

<sup>1)</sup> HIROSE. A nucleus in the human restiform body. Journ. of the Okayama Medical Association. 1920.

<sup>2)</sup> This seems to be in favor of the opinion of MASUDA and BOROWIECKI that the fronto-pontine fibres end in cellgroups situated in front of the cellgroups in which the tempero-pontine tract ends.

SPITZER and KARPLUS hold the opposite opinion (c.f. KAPPERS, l.c. sec. p. 733).

<sup>3)</sup> v. MONAKOW. Der rote Kern, die Haube und die Regio hypothalamica bei einigen Säugetieren und beim Menschen. Arbeiten aus dem neurologischen Institut der Universität Zürich, 1909.

<sup>4)</sup> HORSLEY and CLARKE. On the intrinsic fibres of the cerebellum, its nuclei and its efferent tracts. Brain, 1905.

HORSLEY and CLARKE. Structure and functions of the cerebellum examined by a new method. Brain, 1908.

the median angle of the pes pedunculi (the part called by WINKLER and POTTER <sup>1)</sup> nucl. propius pedunculi). Caudally it is continuous with the grey matter of the pons <sup>2)</sup> which is an evidence of their related function. Frontally it may be followed as far as the globus pallidus, thus proving its relationship to the so called ento- and juxta-peduncular nuclei of reptilia and amphibia. The pes pedunculi in the elephant is also very large in vertical direction and even forces the geniculatum mediale considerably upwards. So it appears that the extrapyramidal motor system is very large in this animal.

Of the *nucl. oculomotorius* in the most caudal sections only the dorso-lateral group is seen, as usually. A little more frontally accedes the ventromedial group.

Frontally the two groups of the nucleus fuse and the nucleus acquires a round form in more frontal sections. About the centre — a little more caudally — appears a new group of cells less intensively coloured, and extending as far as the frontal pole of the nucl. oculomotorii. From this topography we must conclude that this group represents the nucleus *Edinger-Westphal*, serving, according to BROUWER <sup>3)</sup> a. o., for the innervation of the intraocular muscles.

At its frontal pole the nucleus inclines ventrally and above it begins to appear the large *nucleus ellipticus* which I shall describe in detail further on, together with the hypothalamus with which it is connected (see below). A real central *nucleus Perlia* is not present (it also fails in Ungulates).

The nucleus trochlearis is more primitive than in the horse, lying dorsally, on some distance from the nucleus oculomotorius. It is small and sends its root fibres in the typical way around the aquaeductus Sylvii. Ventrally and close to this nucleus runs the fasciculus longitudinalis posterior. Laterally to this nucleus, a small group of cells is found. This may be a reticular nucleus, as often occurs in this region.

In the mid-brain roof on either side of the aquaeductus Sylvii there are rows of large vesicular cells (fig. 8) that are so large that they can be seen with a moderate loupe. They are the cells of the nucleus of the *mesencephalic trigeminus* from which sensory fibers of the masticatory muscles originate (WILLEMS <sup>4)</sup>). The frontal boundary of these cells coincides with the transverse level on which the frontal boundary of the

<sup>1)</sup> WINKLER and POTTER. An anatomical guide to experimental researches on the cats brain (plate XV). Versluys, Amsterdam, 1914.

<sup>2)</sup> An analogous condition seems to exist in the rabbit if we look at Plate XXI of WINKLERS and POTTERS Anatomical guide to experimental researches on the rabbits brain. Versluys, Amsterdam, 1911.

<sup>3)</sup> BROUWER. Klinisch-anatomische Untersuchungen über den Oculomotorius Kern. Zeitschrift f. d. gesamte Neurologie und Psychiatrie, 1917.

<sup>4)</sup> WILLEMS. Localisation motrice et kinesthésique. Les noyaux masticateur et mesencéphalique du trijumeau chez le lapin. Névraze, 1911.

oculomotor root is seen and caudally they can be traced even beyond the level of the nucleus nerv. trochlearis. Their considerable size may be explained by the size of the body, as has been shown by G. LEVI<sup>1)</sup> (for the spinal ganglion cells) and by OBERSTEINER<sup>2)</sup> (for the Purkyně cells). It is very striking to see each cell nearly always seated in a capillary bifurcation. With some cells it seems that the capillaries enter the cell as has been observed with the intra- and supramedullary ganglion cells in *Lophius piscatorius* by STUDNIČKA<sup>3)</sup>.

Behind the tectum, in the lateral lemniscus, that can be well traced from the corpus trapezoides, exactly on the level of the issuing point of the root of the trochlearis there is a well developed nucleus of large cells, the position of which (as in the rabbit) corresponds with the ganglion isthmi (fig. 7 g. i.) of Reptilia. Besides there is a well developed geniculatum mediale (fig. 9 g.m.) which may contain the chief part of the g. isthmi of lower vertebrates, the above named nucleus<sup>4)</sup> being the only part of this ganglion that has kept the original place on the level of the trochlear root, the part included in the ganglion geniculatum mediale having shifted in a frontal direction.

#### *Diencephalon.*

The *geniculatum mediale* commences as a lateral prominence (see fig. 10), a little frontally to the posterior pole of the nucleus ruber. This structure is strongly developed in the elephant, although the cochlear system (see above) is rather small, thus giving a new proof that this ganglion has still other functions than cochlear, viz. being connected with spino-mesencephalic fibres (WALLENBERG<sup>5)</sup>). Frontally the geniculatum mediale leaves the periphery extending in the central grey matter medially to the g. geniculatum laterale in the way as described by INGVAR<sup>6)</sup> approaching the ventral thalamic nuclei. Under it extends a horizontal transverse layer of grey matter lying on the pes pedunculi. This grey substance which I shall call the *nucleus transversus infrageniculatus*, probably

<sup>1)</sup> G. LEVI. I ganglii cerebro-spinali. Supplemento al volume VII dell' Archivio italiano di anatomia e di embriologia, 1908.

<sup>2)</sup> OBERSTEINER. Bemerkung zur Bedeutung der wechselnden Größe von Nervenzellen. Volume giubilare in onore di L. Bianchi, Catania, 1913.

<sup>3)</sup> STUDNIČKA. Ueber die pericellulären und endocellulären Blutcapillaren der Riesenzellen von *Lophius piscatorius*. K.K. Gesellschaft der Wissenschaften. Sitzungsberichte der mathematisch-naturwiss. Classe, 1903.

<sup>4)</sup> This nucleus is commonly called in mammalian brain anatomy nucl. lemnisci lateralis posterioris: c.f. WINKLER and POTTER: An anatomical guide to experimental researches on the cats brain, plate XXI (Versluys, Amsterdam, 1914) and MARBURG's Atlas des menschlichen Zentralnervensystems (Fig. 32) Deuticke, Wien 1910.

<sup>5)</sup> See the general discussion in his paper: Beiträge zur Kenntnis des Gehirns der Teleostier und Selachier. Anat. Anzeiger, Bnd. 31, 1907.

<sup>6)</sup> INGVAR, On thalamic evolution, (page 700). Acta medica Scand., Vol. 59, 1923

representing WINKLER's and POTTER's<sup>1)</sup> c division of the g. geniculatum mediale (fig. 9, 10: nu.tr.i.), extends frontally as far as the geniculatum laterale, a dense layer of fibres separating the structures. Here the nucleus transversus turning in frontal direction laterally and upwards produces a sort of coating for the geniculatum laterale, and finally, extending in front of it, borders the tractus opticus. Some optical fibres pass above this nucleus from which numerous fibres emerge in ventromedial direction. Its function is unknown to me, but its position suggests a relation with the commissura transversa of GUDDEN.

As similar cellgroup occurs in lower fishes, frogs and reptilia.

From the ganglion habenulae the poorly myelinated fasciculus retroflexus (fig. 11) may be easily traced in ventrocaudal direction passing, close in front of the ventral pole of the nucleus ruber and a little medially to it, to the ganglion interpedunculare. Most of the fibres of the fasciculus retroflexus are devoid of myelin, but on its periphery myelinated fibres occur, thus forming a sort of myelin cover for the entire fascicle, as has been described by KAPPERS in fishes (l.c. Bnd. I, p. 80).

The *nuclei anterior and medialis thalami* underneath the ganglion habenulae are clearly separated from the *lateral and ventral nucleus thalami*, and the nuclei medialis thalami of either side are united by a broad *commissura mollis*, in which a distinct *nucleus reuniens* is visible. Frontally the medial nucleus (that cannot be with accuracy separated from the anterior nucleus) extends a little further than the lateral nucleus. A pulvinar (fig. 10 pul.) is present, but relatively small. Ventrally to these nuclei we see the *corpus subthalamicum* from which fascicles of fibres run laterally to the globus pallidus (palaeostriatum) above the pes pedunculi (ansa peduncularis, in the field of *Forel*). It is a circumscribed nucleus, especially so at its medial side (less at its lateral side). Other connections with the striatum are such from the substantia nigra and from the nucleus medialis thalami. The latter connection is distinct along its entire course.

The field of FOREL can be easily distinguished, diminishing caudally where it is more and more replaced by fascicles that near the frontal pole of the nucleus ruber run in a dorsal direction, so that on this level they are longitudinally cut in transverse sections, and are seen passing between the nucleus thalami medialis and lateralis which they separate from one another, and in which to all appearances they enter.

#### *The Hypothalamus and its connections with the oculomotor nucleus.*

When describing the oculomotor nucleus, I mentioned that its frontal pole bends in ventral direction. This displacement is caused by a large cellgroup lying in front of the nucleus (diagram and fig. 9—12, nu.e.). This group touches the raphe, and is separated from the cellgroup of

<sup>1)</sup> WINKLER and POTTER. An anatomical guide to experimental researches on the rabbits brain, Versluys, Amsterdam, 1911 (plate XIX; text page 2).

the other side only by a narrow raphe of grey matter and nerve fibres. Frontally it reaches as far as the thalamus, extending with its frontal pole under the posterior segment of the nucleus medialis thalami. It is ovoid in form, its longitudinal axis running obliquely from behind and above in frontoventral direction. Its transverse form is flattened. Its caudal and central segment come very near the aquaeductus Sylvii and where the nucleus attains its greatest volume, its upper boundary lies close under the aquaeduct of Sylvius, whilst ventrally it reaches as far as the fornix. Ventrolaterally it passes into the central grey matter. In its frontal fourth we may discriminate in it two divisions, a medial and a lateral one that again fuse at the frontal pole. The cells of this nucleus are small and oval.

In front of it and more ventrally the small *c. mammillare* is found. The fornix is clearly seen, sending fibres to the corpus mammillare without however completely exhausting itself. On the contrary, the greater part of its intensively staining bundles extend beyond the mammillare reaching the level of the cellgroup described above, even extending beyond its frontal pole running ventromedially to it. These fibres finish in the nucleus ellipticus (see fig. 12: f. f. a.).

Ventrally to this nucleus, commencing with its frontal pole along its entire length, there is a decussation of commissural fibres between the nuclei of the two sides (fig. 12, com.). Other fibres running in the medial plane of the nucleus can be traced in caudal division in the raphe to the nucleus oculomotorius and nucleus EDINGER-WESTPHAL (fig. 11, X).

Fibres from the nucleus, entering the oculomotorius roots cannot be seen (only at the posterior pole this is less certain). It is to be questioned whether or not this particular nucleus may be homologized with any nucleus described until now in other mammals.

PERLIA<sup>1)</sup> described a nucleus called by him *nucleus medialis anterior* that according to TSUCHIDA<sup>2)</sup> is formed by a group of cells assembled in a little oval form with a dorso-lateral longitudinal axis. Its cells by their size and structure remind us of the cells of the nucleus of EDINGER and WESTPHAL. Some authors regard this nucleus as a proximal continuation of the medioventral group of the nucleus EDINGER-WESTPHAL. In the majority of examined cases TSUCHIDA was able to isolate this nucleus fairly well, and he and also KAPPERS consider the original opinion of PERLIA to be correct to the effect that we have to deal with a cellgroup from which no rootfibres originate. So it may be that the nucleus ellipticus is chiefly an enlarged nucl. medialis anterior.

The homologue of our nucleus certainly occurs in the Cetacea where it has been described as *nucleus ellipticus* by HATSCHEK and SCHLESINGER<sup>3)</sup>

<sup>1)</sup> PERLIA. Die Anatomie des Oculomotorius beim Menschen. Graefe's Archiv f. Ophthalmologie, Bnd. 35, 1889.

<sup>2)</sup> TSUCHIDA. Ueber die Ursprungskerne der Augenbewegungsnerven und über die mit diesen in Beziehung stehenden Bahnen. Arbeiten a. d. Hirnanat. Institut in Zürich, 1905.

<sup>3)</sup> HATSCHEK und SCHLESINGER. Der Hirnstamm des Delphins (*Delphinus delphis*). Arbeiten a. d. Neurolog. Institut der Universität Wien, Bnd. IX, 1902. See also ZWEIG (who saw the same nucleus in *Phocaena*). Jahrb. für Psychiatrie und Neurol. Bnd. 41, 1921.

in the Dolphin. I have also closely examined this nucleus in *Phocaena* and compared its size and its relations to those in the elephant. The only difference is that the nucleus in Cetacea is less flattened in medio-lateral diameter. Moreover in the anosmatic *Phocaena* the fornix is not much developed (and moreover poorly stained in my sections). Hence it was impossible to me to ascertain whether or not fibres of it enter the nucleus ellipticus. On the other hand, however, it was to be seen, also in *Phocaena*, that in the raphe, fibres ascend to the nucleus ellipticus and in *Phocaena* the nuclei of either side are connected by a commissure in exactly the same way as in the Elephant.

It is interesting to note that neither in *Phocaena*, nor in the Elephant it is possible to ascertain a nucleus that would correspond to the nucleus medialis anterior, unless it were the nucl.ellipticus.

That the midbrainbase acts a large part in the search for food in correlation with olfaction is also demonstrated by the presence of the (olfactory) interpeduncular ganglion in all animals in the base of the midbrain. Its relation with vision is expressed by the occurrence of the optic nucl. peduncularis transversus<sup>1)</sup> in this region in birds (nucl. opticus basalis), rodents and ungulates. *Elephas* now gives another striking example of this function, although I could not demonstrate (as I first expected<sup>2)</sup>) a nucl. pedunc. transversus in this animal.

### *Striatum.*

I want to add a few remarks on the *neo-striatum* and *palaeo-striatum* in this animal.

It is easy to discriminate these parts of the basal ganglion. Frontally only the *neo-striatum* is seen, where the nucleus caudatus with its considerably developed frontal pole fuses with the other neostriatal part, the putamen.

Behind this place these segments are separated from each other by the capsula interna but then they fuse once more at the caudal end, where the capsula disappears again. Frontally the *neo-striatum* passes into the nucleus accumbens septi as described by E. DE VRIES.<sup>3)</sup>

Medially to the nucleus caudatus on its ventricular side there is a layer of fibres that form a lining of the third ventricle, analogous to the fasc. fronto-occipitalis, but more complete, forming a thin *capsula intima* (fig. 13, X).

Ventrally to these ventricular fibres the taenia semicircularis runs, lying

<sup>1)</sup> The homology between the nucl. tr. peduncularis transversus of rodents and ungulates with the ganglion opticum basale of birds has been established by KOSAKA and HIRAIWA (Zur Anatomie der Sehnervenbahnen und ihren Zentren, Folia Neurobiologica, Bnd. 9, 1915).

<sup>2)</sup> The nucl. tr. peduncularis transversus in which a basal optic bundle ends, is situated between the ganglion mammillare and the substantia nigra closely to the ganglion interpedunculare in Rodents and Ungulates.

<sup>3)</sup> E. DE VRIES, Das Corpus striatum der Säugetiere. Anat. Anzeiger. Bnd. 37, 1910.

A. PŘECECHTEL: "Some notes upon the finer anatomy of the Brain Stem and Basal Ganglia of *Elephas indicus*".



Fig. 1. Cross section of the cervical cord.

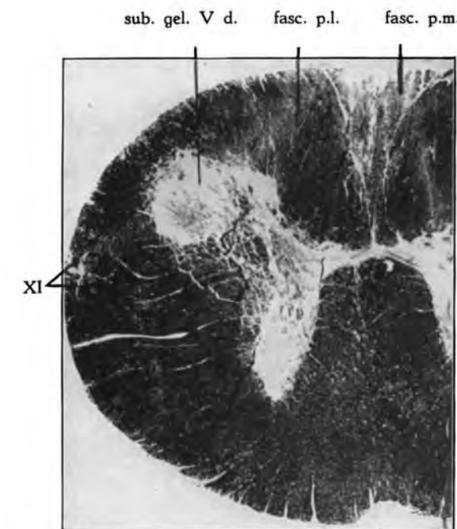


Fig. 2. Cross section of the upper part of the cervical cord.

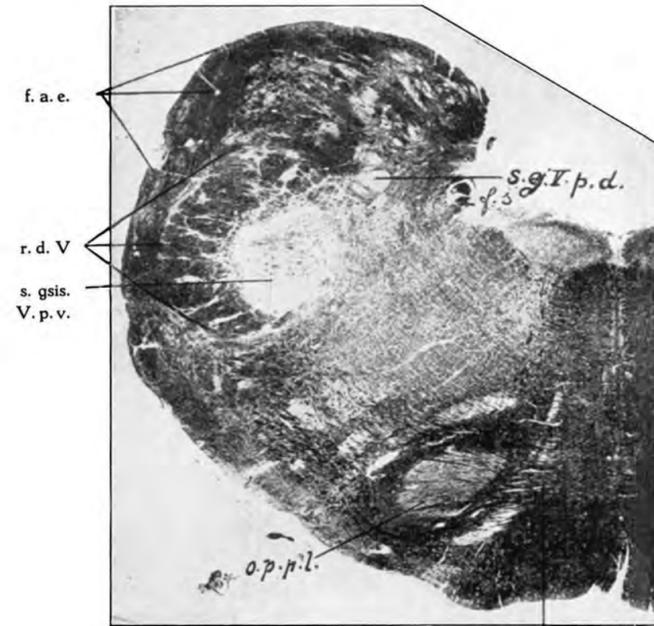


Fig. 3. Section showing the strong development of the fibr. arcuatae externae (f. a. e.) from the nucl. cuneatus externus (Monakow).

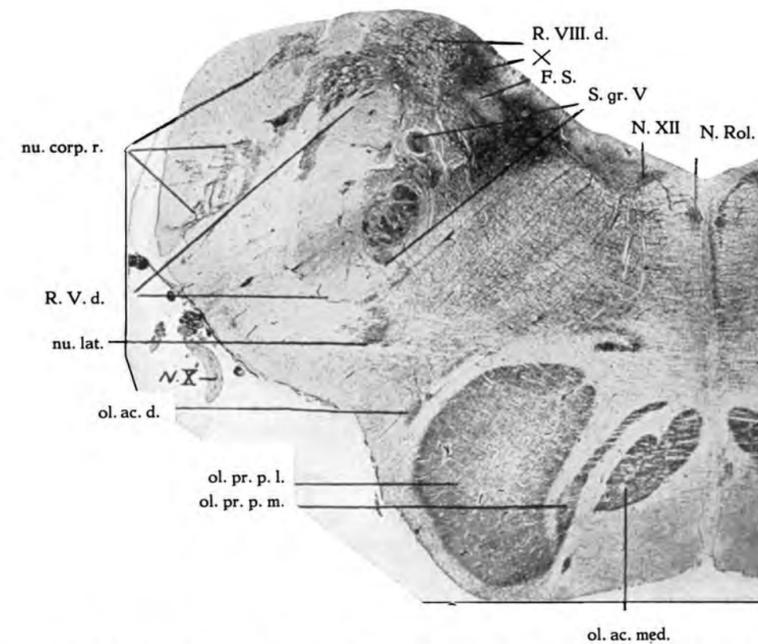


Fig. 4. Section showing the nuclei corporis restiformis (nu. corp. r) and inferior olive.

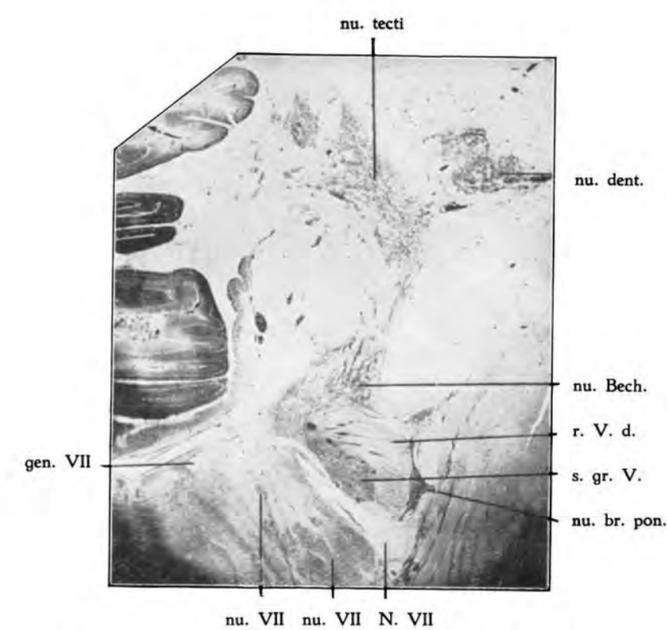


Fig. 5. Nucleus tecti cerebelli and its connection with the nucl. Bechterew. The nucl. brachii pontis and the VII nuclei.

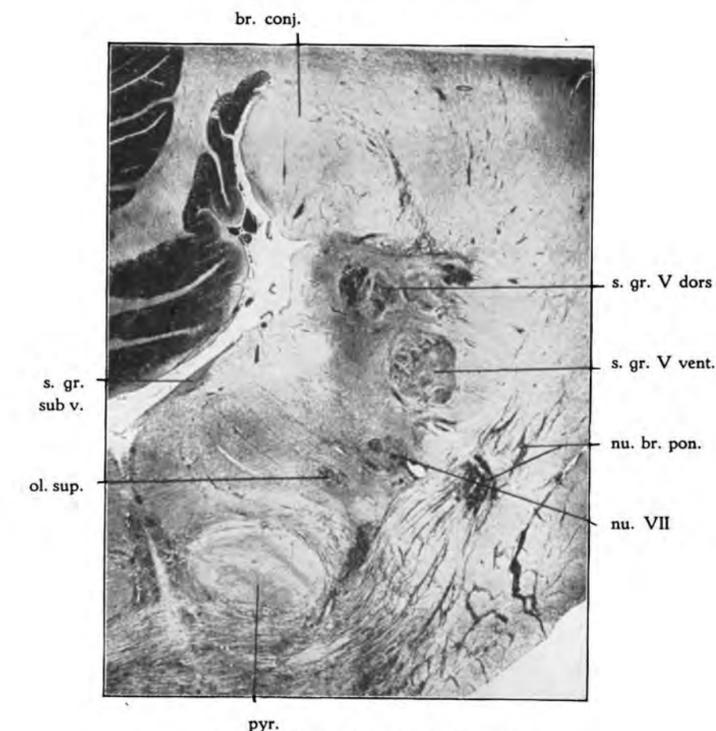


Fig. 6. Showing the nucl. brachii pontis.

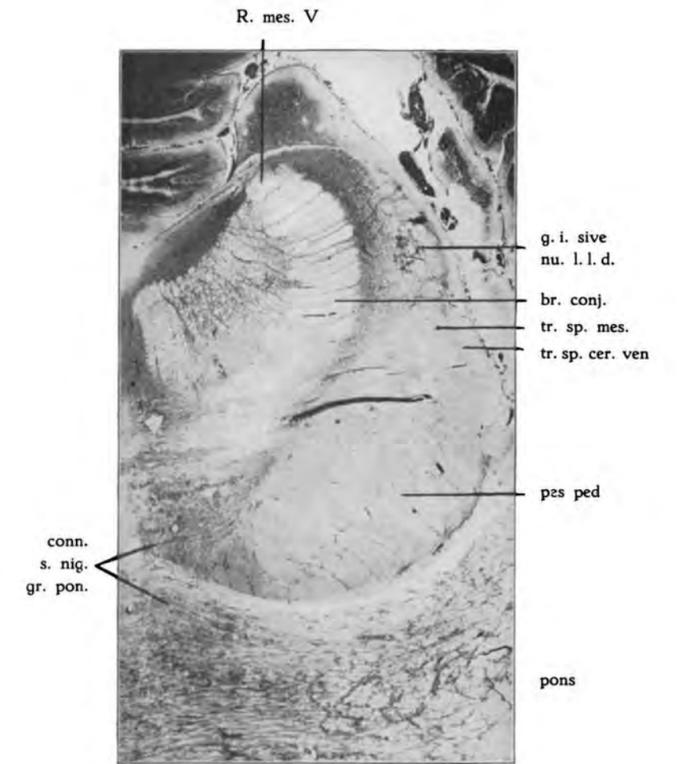


Fig. 7. Showing the connection between the peduncular and pontine nuclei.

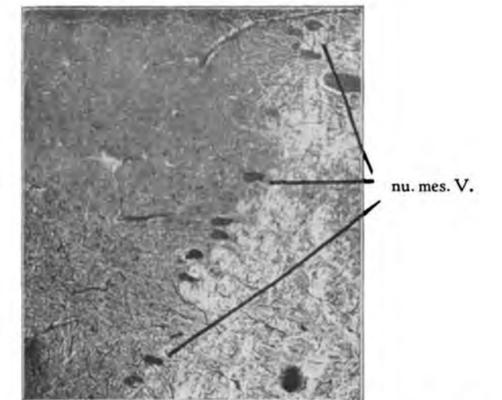
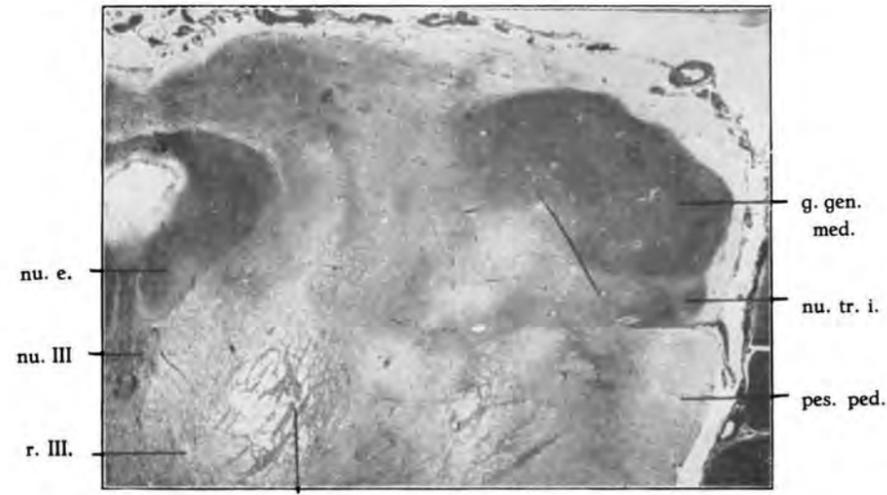


Fig. 8. Nucl. mesencephalicus trigemini. The vascularisation of the cells in seen at the bottom.

A. PŘECECHTEL: "Some notes upon the finer anatomy of the Brain Stem and Basal Ganglia of *Elephas indicus*".



nu. ruber  
Fig. 9. The geniculatum mediale with nucl. transversus infrageniculatus.  
nu. e. = nucl. ellipticus.

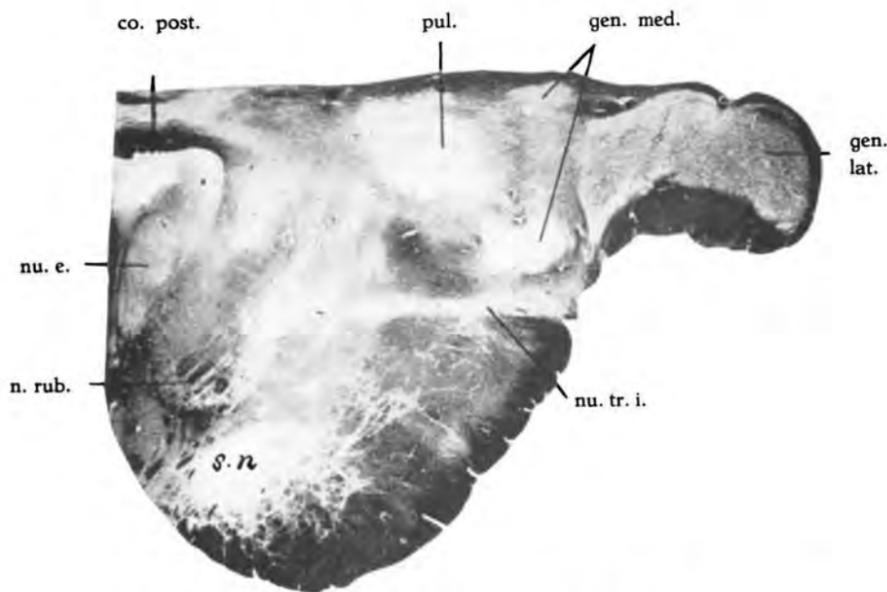
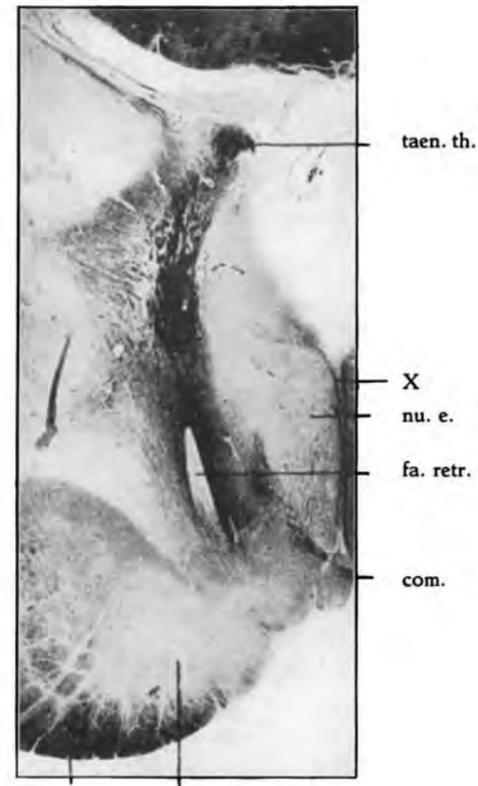


Fig. 10. The nucl. ellipticus (nu.e.); g. geniculata and nucl. transversus infrageniculatus.



pesped. sub. nig.  
Fig. 11. Showing the commissural (com.) and ascending fibres (X) of the nucleus ellipticus (nu. e.).

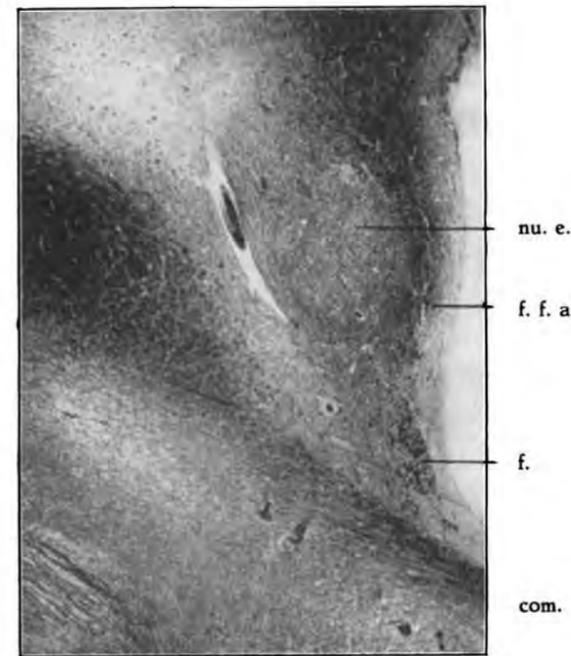


Fig. 12. The fornix (f.) ending with ascending fibers (f. f. a.) in the nucleus ellipticus (nu.e.).

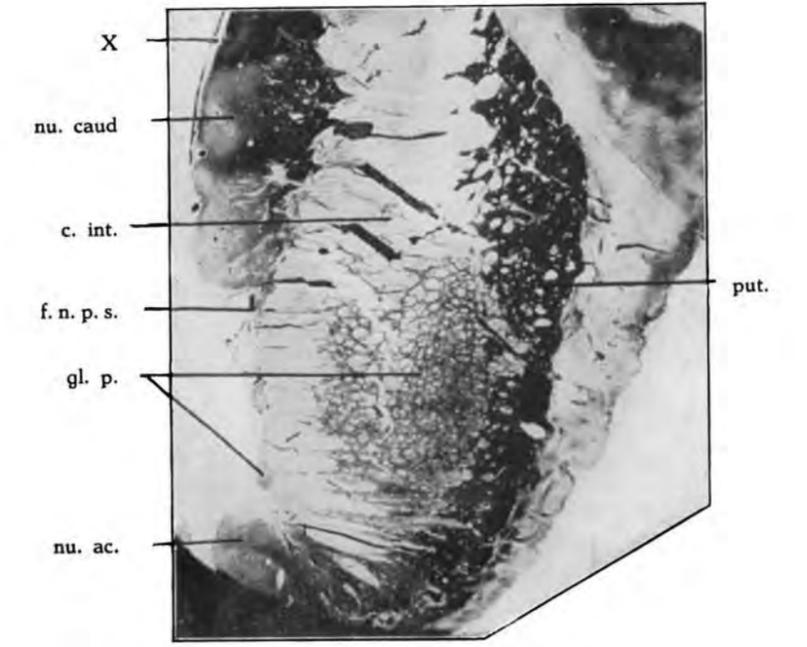


Fig. 13. Showing the subventricular fibers (X) lining the caudate nucleus.  
f. n. p. s. = fiss. neo-palaeo striatica. nu. ac. = nucl. accumbens.

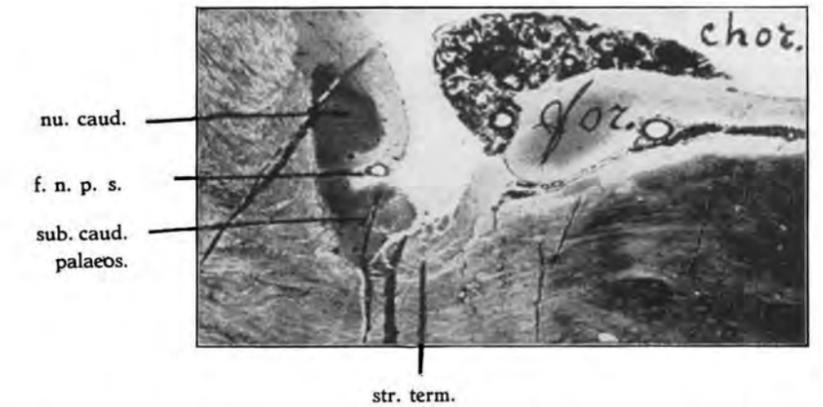


Fig. 14. Cauda nucl. caudati (nu. caud.); fissura neo-palaeostriatica (f. n. p. s.) and substantia palaeostriatica caudata. For. = fornix.

ventromedially against the palaeo-striatum. Originating from the regio parolfactoria and running medially to the striatum the taenia semicircularis can be followed as far as the archistriatum or amygdala as in all other mammals, forming the stria terminalis (fig. 14).

In the elephant, more distinct than in most mammals we find medio-ventrally to the nucleus caudatus (fig. 13) KAPPERS' *fissura neo-palaeo-striatica*,<sup>1)</sup> which clearly runs backward, separating the cauda of the nucleus caudatus from the substantia caudata palaeostratica (fig. 14), the small strip of grey matter extending backward from the globus pallidus or palaeo-striatum.

The relations of this fissure are similar to those, described in other animals and man by KAPPERS, and like there a bloodvessel is found constantly near this fissure. Moreover a medial extension of the lamina medullaris externa — the borderlayer between palaeo- and neo-striatum — is seen on several places near this fissure, also in the Elephant.

The *palaeo-striatum* or *globus pallidus* at its strongest development has the appearance of reticular substance, extending through the capsula interna with small strips to the ventricle. Its relations to the substantia nigra and corpus subthalamicum have been mentioned above. It also takes part in the formation of the nucleus accumbens (fig. 13: nu. ac.).

The claustrum, as described by ERNST DE VRIES<sup>2)</sup> is divided into small islands, that are contiguous with the cortex.

1) ARIENS KAPPERS. The ontogenetic development of the corpus striatum in birds and a comparison with mammals and man. These Proceedings 26, p. 135, 1922, fig. 17). See also Archives Suisses de Neurologie et de Psychiatrie, Vol. XIII, 1923.

2) ERNST DE VRIES. Bemerkungen zur Ontogenie und vergleichenden Anatomie des Claustrums. Fol. Neurobiologica, Bnd. 4, 1910, p. 496.



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**Chemistry.** — "*The oxidative cleavage of fats by fungi*". By H. G. DERX.  
(Communicated by Prof. G. VAN ITERSON JR.).

(Communicated at the meeting of June 28<sup>th</sup>, 1924).

In order to obtain a general insight of the metabolic changes which food undergoes in the living organism, it is necessary to isolate intermediate products which may appear during the decomposition of the food-stuffs. Nevertheless the solution of this problem is not easy, for in the normal healthy organism these intermediate products are often of such transient character that their existence cannot be indicated. In a few cases, however, they have been successfully isolated by the use of various special devices, of which further mention will be made.

The study of the decomposition products of carbohydrates has received most labour and care at the hands of physiologists, and one of the most important recent results to which KLUYVER<sup>1)</sup> has called attention, is the demonstration that in the course of metabolic processes in microorganisms a unity is found that at first sight seems incredible.

For a general review of the various microbiological processes the reader is referred to this highly interesting paper, in which this unity is clearly demonstrated, and I venture to borrow one example from this essay in order to elucidate this point.

It is well known that the investigations of NEUBERG have shown that acetaldehyde is an important intermediary product in the formation of alcohol from sugar by saccharomycetes, but this substance (acetaldehyde) has also been demonstrated during the fermentation of carbohydrates by coli-bacteria (formation of lactic acid, acetic acid, succinic acid, etc.), by butyric acid bacteria (formation of butyric acid, acetic acid, etc.) and by cellulose-decomposing bacteria (formation i.a. of butyric acid, acetic acid, etc.). It has been found that acetaldehyde is also produced in the oxidative cleavage of sugars by the most divergent species of fungi from the group of Mycomycetes (*Monilia candida*, *Oospora lactis*, *Aspergillus cellulosa* B) as well as from the group of Phycomycetes (*Mucor racemosus*, *Mucor rouxii*)<sup>2)</sup>.

A second example is furnished by the investigations of M. MOLLIARD with *Aspergillus niger*<sup>3)</sup>. MOLLIARD demonstrated that, in the oxidation of

<sup>1)</sup> A. J. KLUYVER, Eenheid en Verscheidenheid in de stofwisseling der microben. Chem. Weekbl. 21, 266—277 (1924).

<sup>2)</sup> CLARA COHEN, Bioch. Zeitschr. 112, 139—143 (1920).

<sup>3)</sup> M. MOLLIARD, Compt. rend. biol. 72, 479 (1920), ibid. 87, 967 (1922).

" " C.R. 174, 881 (1920), ibid. 178, 161 (1924).

sugar, it is possible, by regulating the nitrogen or phosphorus in the substrate, to produce either gluconic acid, citric acid or oxalic acid (and — or — carbonic acid) as the chief product. These are substances which, up to the present, have been considered as „specialities” from vinegar bacteria, *Citromyces* species, *Aspergillus niger* and — other fungi. Thus oxalic acid may be formed in considerable quantities, not only by *Aspergillus niger*, but also, under certain circumstances, by different vinegar bacteria<sup>1)</sup>.

These and many other facts point to a gradual cleavage — and in an analogous way — of carbohydrates by widely different microorganisms.

But at the same time it is well known that the conclusions of microbiologists also enter into the domain of animal and vegetable physiology. Very justly animal physiologists suppose that the source of lactic acid in the muscular tissue is to be found in the carbohydrates. Further, G. M. MEYER<sup>2)</sup> found that leucocytes oxidize hexoses (not pentoses) to lactic acid. EMBDEN and his co-workers<sup>3)</sup> found formation of lactic acid in liver rich in glycogen, expressed muscle juice etc. The presence of oxalic acid in urine, in species of *Oxalis* and of *Rheum*, of citric acid in milk and in unripe lemons not only points to the fact that these substances are of general occurrence in nature, but also shows that in all living beings they originate in an analogous way. And there is much truth in the words of MAX RÜBNER, when he says: „Was lebt ist Eins, daher muss trotz der Varianten, welche die einzelnen Spezies vorstellen, in ihrem Leben das gemeinsame Bild des Ganzen sich widerspiegeln.”<sup>4)</sup>

As has already been observed, it is not always easy to detect and to isolate the intermediate products of metabolic processes; generally the oxidation of the food is so intensive that intermediate products are out of the question. This is obvious, for the energy necessary to the organism's growth, reproduction, mechanical labour, etc. is eventually produced by a chemical process, viz. — the combustion of the foodstuffs. The amount of energy set free by this process increases according to the completeness of the oxidation. Incomplete combustion, or in other words, cessation of oxidation by formation of intermediate products, may in a certain sense be considered as a divergence, often brought about by unfavourable physiological conditions, e.g. by lack of oxygen, of assimilable nitrogen etc., in general by unsuitable quantitative or qualitative composition of the food, by temperature sensibly different from that of optimum growth, by the accidental presence of narcotics etc.

Naturally, this does not preclude the existence of special species having

1) ZOPF, Ber. d. deutsch. Bot. Ges. 18, 32, BANNING, Z. f. Bakt. II Abt., 8, 395 (1902).

2) G. M. MEYER, Journ. of biol. Chem. 11, 353—361 (1912).

3) EMBDEN, Bioch. Zeitschr. 45, (1912). Vide also O. HAMMARSTEN, Lehrbuch der physiologischen Chemie, 9th edition, Munich, 1922.

4) MAX RÜBNER, Ernährungsphysiologie der Hefezelle bei alkoholischer Gärung, Leipsic, 1913, page 1.

permanently weak oxidative capacity even under the most favourable conditions; on the contrary, it points to the possibility that such hereditarily constant forms originate from adaptation to definite nutritional conditions. Compare e.g. *Acetobacter xylinum*, BROWN and *Acetobacter suboxydans*, KLUYVER and DE LEEUW<sup>1)</sup>).

But, on the other hand, it is certain that *Saccharomycetes* thrive only when a sufficient supply of oxygen is at their disposal:

Under these circumstances an important part is played by the oxidative cleavage of sugar to carbonic acid and water, and on account of the vigorous growth of the yeast an apparently increased production of alcohol is observed. In a similar way an accumulation of oxalic acid in cultures of *Aspergillus niger* is possible only when there is a lack of assimilable nitrogen, or when growth takes place at lower temperatures. Under favourable circumstances there is very little formation of oxalic acid.<sup>2)</sup>

In consequence, I am of opinion that a wider meaning may be taken from the words of DUCLAUX regarding the formation of oxalic acid: „C'est un produit de souffrance". This will appear more clearly in the subsequent course of my paper.

So far, views on the oxidation of fats in the living organism have been expressed rather by zoological physiologists than by microbiologists, though this is not the case with the oxidation of carbohydrates. This is clearly shown by the work of PIERRE WORINGER<sup>3)</sup> and by the voluminous list of the literature he mentions. As the oxidation processes in the higher animals and in microorganisms are analogous it may be interesting to trace the methods applied by physiologists in these researches. We find here five fundamentally different methods of procedure:

1. The indirect method, consisting of the investigation of the oxidative capacity of the organism in respect to intermediate products theoretically possible.

2. The introduction into the molecule of a group difficult to oxidize, e.g. the benzene nucleus, in order to prevent complete combustion.

3. The perfusion of isolated surviving organs.

4. Administration of the substance under investigation to individuals having definite pathological disturbances of the dissimilation processes, e.g. diabetics (induced or otherwise), alcaptonurics, etc.

5. Subcutaneous or intravenous injections of large quantities of the substance to be investigated.

The methods given under headings 1. and 2. and sometimes 3. (expressed juices) can be applied to microorganisms.

One of the fundamental results of the above mentioned investigations is the discovery that the oxidation of normal fatty acids commences at

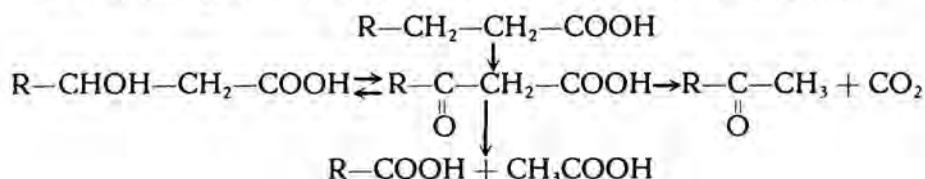
1) A. J. KLUYVER en DE LEEUW, Tijdschr. v. Verg. Geneesk., 10, Afl. 2-3 (1924).

2) EMMERLING, Z. f. Bakt. II Abt., 10, 274 (1903).

3) P. WORINGER, La dégradation des acides gras dans l'organisme animal, Paris, MASSON & Cie.

the  $\beta$ -carbon atom with formation of a ketonic acid. The latter splits off acetic acid, so that a fatty acid with two C atoms less than the original fatty acid results, and so on<sup>1)</sup>. The  $\beta$ -ketonic acid may under certain circumstances be reduced to a  $\beta$ -hydroxy acid, the action being reversible. On the other hand  $\text{CO}_2$  may be split off with the formation of methyl-ketone, but this must be considered an abnormal decomposition product.

The following scheme demonstrates the reactions under discussion:



### Experimental.

If we introduce mould spores into a RAULIN-DIERCKX solution<sup>2)</sup> which contains ammonium nitrate and ammonium phosphate as source of nitrogen,

TABLE I.

Fungus: *Penicillium cyclopium*<sup>3)</sup>; Nutrient medium: Raulin-Dierckx solution.  
T = 22°–25° C.

Substance added	Butyric acid	Valeric acid	Caproic acid	Caprylic acid	Capric acid	Lauric acid	Myristic acid	Palmitic acid	Stearic acid	Oleic acid	Elaidic acid	Brassicic acid	Control
As fatty acid	—	—	—	—	( $\mp$ ) K	$\pm$ K	+	++	++	+	++	++	+
As K-salt	+	+	$\pm$ K	$\mp$ K	( $\mp$ ) K	( $\mp$ ) K	$\mp$ K	$\pm$	+	+	+	+	+

Signs: — no growth; ( $\mp$ ) very feeble growth after 2 weeks;

$\mp$  very feeble growth;  $\pm$  feeble growth; + vigorous growth;

++ very vigorous growth; K formation of Ketones.

<sup>1)</sup> Compare F. KNOOP, Beitr. z. chem. Phys. u. Path. **6**, 150 (1905), **11**, 411 (1908).

<sup>2)</sup> Vide PH. BOURGE, Les moisissures du groupe *Penicillium* Link, La Cellule **33**, 43 (1923). The preparation is as follows:

1. Dissoudre 0,40 de carbonate de magnésic dans une fiole jaugée de 100 c<sup>3</sup> au moyen de 0,71 d'acide tartrique.
2. Dans un ballon jaugé d'un litre, contenant 800 à 900 gr. d'eau distillée, dissoudre: saccharose 46,6; nitrate d'ammoniaque 2,66; phosphate d'ammoniaque 0,40; carbonate de potassium 0,40; sulfate d'ammonium 0,16; sulfate de zinc 0,04; sulfate ferreux 0,04.
3. Ajouter 66–67 c<sup>3</sup> de la solution de tartrate magnésique et compléter jusqu'au trait de jauge.

<sup>3)</sup> A very common kind of the long series of blue-green *Penicilliums*, which are always erroneously indicated by the generic name of "*Penicillium glaucum*".

and saccharose as source of carbon, and add  $\frac{1}{4}\%$  of fatty acid in the one case and  $\frac{1}{4}\%$  of the corresponding potassium salt in the other, we are able, after leaving the cultures for four days at 22–25° C. to demonstrate the results drawn up in table I (page 99).

This table shows at a glance that the lower fatty acids, up to and including lauric acid, hinder the growth very markedly. It must, however, be taken into consideration that the acids from caprylic upwards do not completely dissolve under the experimental conditions, but even lauric acid, which is almost insoluble in water, has a decidedly preventive action on growth. The higher solid fatty acids, on the contrary, appear to exert a favourable influence. But in this case the floating particles of fatty acid tend to act mechanically as a support for the mycelium rather than as a nutritive substance.

These results are quite in accord with TRAUBE's rule, but are somewhat obscured by the unfavourable influence caused by the increase of the H-ion concentration of the lower acids (brought about by their greater solubility). In the investigations with potassium salts, where the  $P_H$  at the commencement of the experiment was always regulated to 6 to 7, the latter influence did not appear and TRAUBE's rule held good in every respect<sup>1)</sup>. The fatty acids formed by hydrolysis of their salts are adsorbed on the mycelium:

In the case of potassium caproate enough free undissociated caproic acid is present in the liquid to markedly hinder oxygen resorption by the adsorption of the acid on the young submersed mycelium. This is also the case with the caprylate, caprate, laurate and myristate of potassium, whereas, with the salts of the higher acids, notwithstanding their hydrolysis, the concentration of free fatty acid in the aqueous solution is too small to appreciably obstruct oxygen assimilation. The normal growth in the case of the higher soaps shows at the same time that only the fatty acid molecules in the solution have a narcotic action, and not the soapmicels or other complexes. The assimilation of oxygen is thus impeded (and this is in agreement with the ideas of WARBURG<sup>2)</sup> regarding surface catalysis) by this adsorption of fatty acids on the young submersed mycelium and, consequently, oxidation of food-stuffs (sugar and fatty acid) is strongly checked. And in fact Table I shows that ketones are formed in every case where growth is impeded, but not completely prevented. These ketones may be isolated by distillation, followed by neutralisation and extraction with ether, and may be identified as semi-carbazones. This showed that each fatty acid gave rise to one specific ketone, thus:

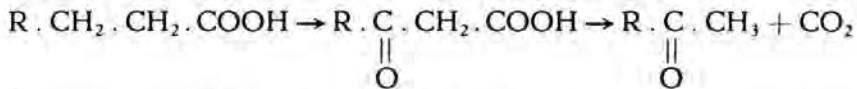
1) Oleic acid, Elaïdic acid, and Brassidic acid do not belong to this homological series. This is perhaps the cause of the anomalous behaviour of oleic acid and its potassium salt.

2) Compare H. FREUNDLICH, *Kapillarchemie*, 2, Auflage, Leipsic 1922.

caproic acid	yielded	methyl-propylketone
caprylic acid	„	methyl-amylketone
capric acid	„	methyl-heptylketone
lauric acid	„	methyl-nonylketone.

In the case of myristic acid the quantity of ketone formed was too small for analysis, but we may doubtless assume that myristic acid will give rise to methyl-undecylketone.

The result is thus unequivocal. In no other way can we demonstrate so clearly that oxygen attacks at the  $\beta$ -position in the molecule. As was to be expected, the reaction takes the following course:



But once more I wish to emphasize the fact that this formation of ketones manifests itself only when growth is impeded, and that ketones are not normal intermediate products in the biological oxidation of fatty acids: „Ce sont des produits de souffrance.”<sup>1)</sup>

If we attempt to isolate the volatile ketones in duplicate cultures about ten days old, we find that they have disappeared. This disappearance is found to occur pretty well at the time when the mycelium raises itself in the air, begins to form conidiophores and puts forth the green conidia.

Evidently respiration is no longer impeded, growth becomes normal, and the ketones (which also have a narcotic action) are further broken up.

The formation of ketones is not restricted to free fatty acids and their soaps; fats themselves may lead to the formation of ketones. It follows, however, from the preceding work that the formation of ketones is to be expected only in such fats as contain the lower fatty acids. The best known of these fats are coconut oil (*Cocos nucifera*), palm-kernel oil (*Elaeis guineensis*), babassu oil (*Attalea funifera*), cohune oil (*Attalea cohune*), and a few other fats obtained from seeds of various species of palm, and finally butterfat.

For the purposes of this paper we shall restrict ourselves to coconut oil and butterfat.

Older investigations show that it is extremely probable that the primary action of a fungus on neutral fat is a splitting into fatty acid and glycerine by a mould lipase. Such lipase is usually present in the substrate of *Penicillium* cultures and can readily be demonstrated by well-known processes. Further, it is certain that glycerine can serve as a source of carbon for most fungi, but the fatty acids will, or will not, have a narcotic action, according to the conditions and to their places in the homologous series. The following experiments may serve as an illustration.

Three species of *Penicillium*, all generally designated as „*Penicillium*

<sup>1)</sup> DUCLAUX, loc. cit.

"glaucum" were tested using the saccharose containing RAULIN-DIERCKX solution to which 1 0/0 of coconut oil had been added.

TABLE II <sup>1)</sup>.

	Raulin Dierckx + 1 0/0 coconut oil	Control without coconut oil
Penicillium cyclopium Westling.	+	+
.. leucopus Biourge.	± K	+
.. Roquefort Thom.	+	+

These results show that *Penicillium leucopus*, Biourge produces so much fatty acid — evidently on account of a very vigorous lipase activity — that its growth is suppressed. Only in this instance is ketone produced, no trace whatever of ketone being formed with the other *Penicillia*. <sup>2)</sup> Should the medium contain only inorganic salts and coconut oil with no saccharose <sup>3)</sup> the results are entirely different.

TABLE III <sup>1)</sup>.

	Inorganic nutrient medium + 1 0/0 coconut oil	
	After 4 days	After 14 days
Penicillium cyclopium Westling.	± K	++
.. leucopus Biourge.	± K	++
.. Roquefort Thom.	± K	++

In these experiments all three species formed ketones. In this medium glycerine is the source of carbon, being formed together with about seven times its weight of fatty acids by the action of the mould lipase. Under these unfavourable circumstances it is evident that ketones must be formed. But at the same time the experiments show that here also after the lapse of two weeks ketones had entirely disappeared.

If these experiments are now repeated using butterfat instead of coconut oil in the same inorganic medium no trace of ketone can be detected,

<sup>1)</sup> For explanation of the signs see Table I.

<sup>2)</sup> This shows how the use of the collective name of "*Penicillium glaucum*" may give rise to contradictory data in the literature. Such contradictions are indeed very frequent.

<sup>3)</sup> This nutrient medium, which was also used for the other experiments mentioned, contains: Water 1000; Ammoniumnitrate 2,5; Ammoniumphosphate 0,5; Monopotassium-phosphate 0,5; Magnesiumsulphate 0,5; Zinxsulfate 0,04; Ferrosulfate 0,04; parts by weight.

even under these unfavourable biological conditions. This, at first sight unexpected, result is to be explained by the difference in composition of coconut oil and butterfat.

TABLE IV.

	Fatty acids from coconut oil <sup>1)</sup>	Fatty acids from butter <sup>2)</sup>
Butyric acid . . . . .	—	± 3.6 %
Caproic acid . . . . .	2 %	± 1.9 %
Caprylic acid . . . . .	9 %	± 0.7 %
Capric acid . . . . .	10 %	± 1.4 %
Lauric acid . . . . .	45 %	± 6.0 %
Myristic acid . . . . .	20 %	± 18.7 %
Palmitic acid . . . . .	7 %	± 29.5 %
Stearic acid . . . . .	5 %	± 5.4 %
Oleic acid . . . . .	2 %	± 32.8 %
Dioxy-oleic acid . . . . .	—	

Coconut oil thus contains about 5 times the quantity of volatile, ketone-forming fatty acids contained in butterfat. It need hardly be pointed out that this is of great importance when we take into consideration the fact that the fatty acids, liberated by lipase, partly remain in solution in the fat. Yet it can scarcely be doubted that under still more unfavourable conditions, e.g. by culture in an atmosphere deficient in oxygen, or by symbiotic culture with a vigorous fat-splitting organism, ketones may also appear in butterfat.

The ketones formed from fatty acids all have a very characteristic odour, which is particularly intensive in the cases of methyl-propyl-, methyl-amyl- and methyl-heptyl-ketones so that in investigations with the odourless coconut oil the appearance of this odour may be considered a very sensitive reaction for ketone-formation. These strongly odoriferous substances have from time to time attracted the attention of investigators and the following is a short summary of our present knowledge regarding them.

HALLER and LASSIEUR <sup>3)</sup> found in the unsaponifiable part of coconut

<sup>1)</sup> ELSDON, *Analyst*, **38**, 8 (1913).

<sup>2)</sup> Means of analyses published by KOEFED, *Analyst*, **17**, 130 (1892). BROWNE, *Journ. Am. Chem. Soc.* **21**, 807, (1899), and HOLLAND and BUCKLEY, *Journ. Agric. Research* **12**, 719 (1918).

<sup>3)</sup> HALLER and LASSIEUR, *Compt. rend.* **150**, 1013 (1910), **151**, 697 (1910).

oil traces of an unknown aldehyde, methyl-n-nonyl ketone (75 %), methyl-n-heptyl ketone, methyl-n-undecyl ketone (small quantity) and methyl-n-heptyl- and methyl-n-nonyl carbinols. The alcohols, together amounting to 12 %, were optically active and dextro rotatory <sup>1)</sup>).

G. H. SALWAY <sup>2)</sup> found  $\pm 1.1$  % of volatile unsaponifiable constituents, consisting principally of methyl-nonyl ketone, in a sample of palm-kernel oil. This was confirmed by SCHIMMEL and Cie <sup>3)</sup>, who detected also methyl-amyl- and methyl-heptyl ketones.

These fats and the nature of the ketones found corroborate the experimental results. It is, therefore, very probable that these various substances detected in coconut- and palm-kernel oils are formed by fungi. ORLA JENSEN's <sup>4)</sup> paper on the rancidity of butter shows that several investigators had unconsciously caused the formation of ketones in their experiments with fungi on fats. JENSEN demonstrated that when butter became rancid "esters" appeared (ethyl-butyrate,) this being in agreement with the results of AMTHOR <sup>5)</sup>, who, however, found in addition to esters in rancid butter, other substances which were unsaponifiable. These were undoubtedly ketones. Two fungi in particular were responsible for the formation of "esters" (ketones):

1. *Cladosporium butyri*, ORLA JENSEN; This organism, according to my observations is not a cladosporium, but belongs rather to the group of saprophytic monilia; it forms real esters not only in butter, but also in nutrient media containing glycerine or carbohydrates.

2. *Penicillium glaucum*: <sup>6)</sup> This fungus did not produce „esters" in a culture medium, but did so when grown along with *Oidium lactis* on butter. This increased „ester" formation, noted also when *Oidium lactis* and *Cladosporium butyri* were grown together, is no longer to be wondered at; *Oidium lactis* has powerful lipolytic properties and by reason of the marked formation of free fatty acids narcotizes *Cladosporium butyri* and *Penicillium glaucum* so that ketones are now formed. The following sentence by JENSEN is conclusive: "Die mit *Penicillium* geimpfte Butter roch nämlich bei der Distillation deutlich nach Amyl-butyrat und vielleicht auch nach Aethyl-butyrat." <sup>7)</sup> The odour of methyl-amyl ketone and that of amyl-butyrate are similar, but the odour of the ketone is the more ethereal. ORLA JENSEN also observes that lactose represses "ester" formation.

H. C. JACOBSEN <sup>8)</sup>, who experimented with vegetable fats, confirmed

<sup>1)</sup> The carbinols are formed from the ketones by biological reduction. Cf. the reduction of methyl-nonylketone to dextro-rotatory methyl-nonylcarbinol by fermentation, by C. NEUBERG and F. F. NORD, Ber. **52**, 2237-48 (1919).

<sup>2)</sup> G. H. SALWAY, Journ. Chem. Soc. **111**, 407 (1917).

<sup>3)</sup> SCHIMMEL and Cie, Ref. Seifensieder Ztg. (1919) 496.

<sup>4)</sup> ORLA JENSEN. C.f. Bakt. II Abt. **8**, (1902).

<sup>5)</sup> AMTHOR. Zeitschr. f. Anal. Chemie (1899) p. 10.

<sup>6)</sup> Vide page 7, note 2.

<sup>7)</sup> ORLA JENSEN, loc.cit. page 369.

<sup>8)</sup> H. C. JACOBSEN, Folia Microbiologica, **5**, Part 2, (1918).

the formation of "esters" by the action of fungi on coconut oil on the basis of JENSEN's work. Besides his *Penicillium glaucum* and *Cladosporium butyri* Orla Jensen, also *Aspergillus* spec., *Mucor* spec., *Clasterosporium* spec., *Hormodendron* spec., and *Phoma* spec. gave rise to the formation of „esters". *Oidium lactis* did not produce „esters".

The investigation of W. N. STOKOE <sup>1)</sup> appeared in 1921. Though he did not explain the way in which ketone formation is brought about, he has been the first to explain the exact constitution of the products which cause this rancidity. He grew the fungi on an emulsion of coconut oil and gelatine lactose medium with the result that the formation of ketones took place only with coconut- and palm-kernel oils, not with butterfat. Contrary to JACOBSEN he found that only *Penicillium* and *Aspergillus* species produced "perfume rancidity" i.e. ketone formation. <sup>2)</sup> *Botrytis cinerea*, *Mucor mucedo*, *Cladosporium oidium* and *Oidium lactis* did not form ketones.

This discrepancy is no doubt due to the fact that JACOBSEN experimented on a poorer nutrient medium than that used by STOKOE, for it has been shown that *Penicillium cyclopium* and *Penicillium Roquefort* formed ketones only in an inorganic medium using coconut oil as the sole source of carbon, but grew without ketone formation in the saccharose-containing RAULIN-DIERCKX solution. JACOBSEN's results are supported by the following experiments in which different fungi were tested with regard to their ketone-forming capacity at a temperature of 23° C. using an inorganic medium in which coconut oil was the sole source of carbon. After a period, the length of which depended on the rate of development, the formation of ketones was demonstrated with the following fungi:

*Penicillium leucopus* Biourge, *P. cyclopium* Westling, *P. flexuosum* Dale, *P. rubrum* Stoll?, *P. baculatum* Westling, *P. Roquefort* Thom, *P. brevi-compactum* Dierckx, *P. (Citromyces) Pfefferianum* Wehmer, *P. (Scopulariopsis) brevicaulis* Saccardo, *Aspergillus glaucus* (Link?), *Asp. minimus* Wehmer(?), *Asp. flavus* Link, *Asp. albus* Wilhelm, *Asp. niger* van Tieghem, *Asp. fuscus* Bonorden(?), *Cladosporium herbarum* Link, *Monilia Australica* Derx nov. spec., *Monilia (Cladosporium) butyri* Orla Jensen, *Sporodesmium* spec., *Trichoderma Koningi* Oudemans(?), *Hyalopus* spec.

Formation of ketones was not observed in experiments with:

*Penicillium italicum* Wehmer, *Oospora (Oidium) lactis* Fresenius, *Thielaviopsis ethacetica* Went, *Catenularia fuliginea* Saito, and *Penicillium digitatum* Saccardo.

<sup>1)</sup> W. N. STOKOE, Journ. Soc. of Chem. Ind. **40**, 75—81, (1921).

<sup>2)</sup> STOKOE is of opinion that from *Penicillium* cultures he has isolated an exo-enzyme which splits coconut-oil with formation of ketones. Some objections, however, may be raised against his method of procedure; up to this moment I have not yet succeeded in isolating such an enzyme. The views, mentioned above, on the narcotic action of fatty acids on the respiratory functions of the mycelium do not make the appearance of an oxidative exo-enzyme more probable.

Two groups of these fungi showing a negative reaction can be distinguished; 1. those showing hardly any growth under the experimental conditions, and which need therefore no discussion, and 2. those growing well under the same conditions. To the latter group belong *Penicillium italicum* Wehmer, and *Oospora lactis* Fresenius. No doubt the conditions are still too favourable in this case, for if *Penicillium italicum* is grown in a RAULIN-DIERCKX solution, containing saccharose and to which  $\frac{1}{2}\%$  of potassium caproate is added, formation of methyl-propyl ketone is observed. Under these conditions *Oospora lactis* does not grow at all.

Thus there is only a quantitative difference between these fungi as regards their ketone-forming capacity. With the exception of *Oospora lactis* in every case ketone formation could be experimentally demonstrated. Not can it be attributed to chance that *Oospora lactis* is an exception; its very vigorous fat-splitting and oxidizing properties are well known. The organism also appears to offer a strong resistance to antiseptics<sup>1)</sup>. These facts give a better insight as to the reason of the non-ketone-forming capacity of *Oospora lactis*.

It is a remarkable fact that the above mentioned ketones occur naturally in other substances; the ethereal oil from *Ruta graveolens* consists to the extent of 90% of a mixture of methyl-nonyl- and methyl-heptyl ketones; the ethereal oil from the leaves of *Citrus limetta* also contains methyl-nonyl ketone. Methyl-amyl ketone is present in the ethereal oil from the bark of *Cinnamomeum Zeylanicum* and in the oil from the flower-buds of *Eugenia caryophyllata*. And these are precisely the ketones formed by fungi, e.g. from coconut oil. The probability is therefore enhanced that they are formed in the same way in plants, i.e. by imperfect oxidation of fatty acids. Finally we may point to the chemical analogy of this reaction viz. the demonstration by DAKIN<sup>2)</sup> that methyl ketones are formed when the ammonium salts of fatty acids are treated with hydrogen peroxide. In this purely chemical process, too, the oxygen attacks the molecule at the  $\beta$ -position.

## SUMMARY.

1. Stress is laid upon the great analogy existing in the fermentative and oxidative processes of microorganisms, higher plants and animals.
2. The formation of methylketones in the cleavage of fatty acids by fungi proves that in this case also oxygen attacks the  $\beta$ -carbon atom.
3. The fatty acids, up to and including myristic acid, are adsorbed on the mycelium of fungi, and exert a more or less depressing effect on their respiratory functions. This is the reason the oxidation of these fatty acids cannot extend beyond the corresponding ketonic acids, which, at this point, perhaps under the influence of a carboxylase, decompose into carbonic acid and a methylketone. At the same time it follows that the formation

<sup>1)</sup> Vide LAFAR, Handb. d. Techn. Mykologie, IV, 344, Jena (1907).

<sup>2)</sup> DAKIN, Journ. of biol. Chem. 4, 221, 227, 225 (1908).

of ketone only appears under unfavourable conditions. The ketones are not normal intermediate products in the oxidative cleavage of fats.

4. Almost all fungi can form ketones, the only exception so far found being *Oospora lactis*; probably this is to be attributed to the very vigorous oxidizing properties of this fungus.

5. In fungi, as in the higher animals, the process of the oxidative cleavage of fats is analogous. As the same methylketones are found in different ethereal oils this process probably takes the same course in plants also.

*Delft. June, 1924.*

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**Chemistry.** — *"The Influence of Pressure on the Solubility of Substances V. The system Naphtalene-Tetrachlorethane"*. By Prof. ERNST COHEN, WILHELMA A. T. DE MEESTER, and Dr. A. L. TH. MOESVELD.

(Communicated at the meeting of October 25, 1924).

1. The investigations <sup>1)</sup> on the influence of pressure on the solubility of substances have taught that this influence is relatively small, compared with the effect of temperature. Yet a few cases are known in which the effect of pressure is very considerable, and so the question arises: how does in these cases the solubility depend on pressure?

Theoretical considerations, to which we shall revert directly, show that great effects are to be expected only in those cases in which pressure diminishes the solubility. Considering that the decrease with increasing pressure must become smaller, the question arises, whether the solubility will pass through a minimum, or with increasing pressure will asymptotically approach a definite value.

In one of our former investigations <sup>2)</sup> it was shown that the results of the determinations of solubility could very well be represented by a parabolic curve, so that the existence of a minimum could be made plausible. This, however, lay outside the range investigated experimentally. As, moreover, it would occur at a pressure more than twice as great as the highest at which measurements had been carried out, great value cannot be attached to this extrapolation. So it was of importance first of all to find a system of substances which was more suitable for such an investigation.

2. Two ways are open to find such a system: If it is possible to find by a theoretical method the conditions which must be satisfied in order to get a strongly curved solubility curve, such a case can be investigated directly. As, however, the curving of this line depends i.a. on the compressibilities of the solute and the saturated solution, and data on this subject as regards the solute, don't practically exist, while the determination of these values takes much time, and so does not lend itself at all

<sup>1)</sup> Zeitschr. f. physik. Chemie **67**, 432 (1909); **69**, 102 (1909); **75**, 257 (1910); **93**, 385 (1919); **94**, 210 (1920); **104**, 323 (1923); **105**, 155 (1923); Journ. Amer. Chem. Soc. **38**, 2632 (1916). Thesis CASTEELS, Neuchatel, (1920).

<sup>2)</sup> Zeitschr. f. physik. Chemie **93**, 385 (1919), especially page 433 et seq.

to preliminary investigations, we have followed the second method, which leads us to find systems in which pressure has great influence on the solubility.

In such a case the solubility curve must soon curve when the pressure is increased, as otherwise negative values of solubility would have to appear. In order to find such systems it is only necessary to determine the fictitious change of volume which accompanies the process of solution, for which several different methods are at our disposal<sup>1)</sup>. But even in those cases, in which the influence of pressure on the solubility is slight, a minimum may be expected, as the same curvature of a curve directed slightly downward, makes the curve slope upwards again at a much smaller pressure.

3. If we do not take into consideration the complications which arise when the vapour of the saturated solution does not follow RAOULT'S law, we may write:

$$\frac{dl \cdot c}{dp} = -\frac{\Delta v}{RT}$$

in which  $c$  is the concentration of the substance dissolved in mol.  $^{\circ}/_0$ ,  $p$  the pressure,  $T$  the temperature,  $\Delta v$  the fictitious change of volume at  $T$  and  $p$ , and  $R$  the gas constant.

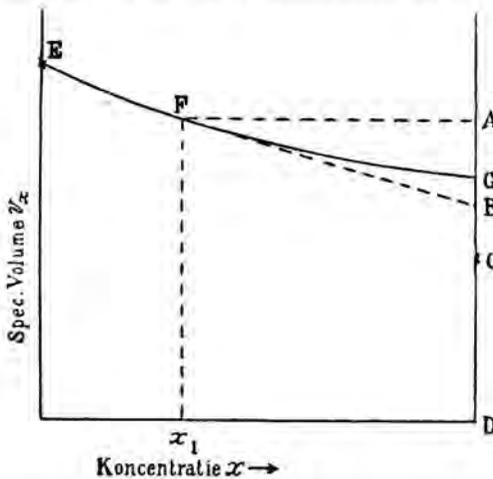


Fig. 1.

The form of the curve which represents the solubility as function of the pressure is now determined by the value of  $\Delta v$  as function of the pressure:

$$\frac{d(\Delta v)}{dp} = \frac{\partial(\Delta v)}{\partial p} + \frac{\partial(\Delta v)}{\partial c} \frac{\partial c}{\partial p}$$

The first term of the right hand of the equation represents the change which  $\Delta v$  undergoes with pressure as a consequence of the difference in compressibility of the solid and its melt (assumed to be in a subcooled state). The second term relates to the change with pressure (and the concentration) of the volume change on mixing the solvent and the solute (subcooled). This is easily seen in Fig. 1<sup>2)</sup>. For, at a higher pressure, the curve  $EFG$  as well as the point  $C$  lie lower. Moreover  $EFG$  does not remain parallel to itself, while the point  $F$  is also displaced.

<sup>1)</sup> Zeitschr. f. physik. Chemie **105**, 145 (1923).

<sup>2)</sup> See concerning this figure also Zeitschr. f. physik. Chemie **93**, 385 (1919), especially par. 66.

If we assume, as a first approximation, that  $\Delta v$  is a linear function of the pressure:

$$\frac{dl \cdot c}{dp} = a + \frac{\beta p}{RT}$$

or at constant temperature:

$$\frac{dl \cdot c}{dp} = A + Bp$$

$$l \cdot c = Ap + \frac{B}{2} p^2 + C.$$

Depending therefore on the sign and the value of the coefficients there is a possibility for a minimum in the solubility. However, it is also possible that the solubility curve runs asymptotically. If we pay attention only to the influence of the compressibilities on the value of  $\Delta v$  it is highly possible that  $\Delta v$  does not depend linearly on pressure, but approaches to zero when the pressure increases. The investigations of BRIDGMAN<sup>1)</sup> have shown that the change of volume on melting (this, however, is only one term of  $\Delta v$ , unless the process of dissolving in the saturated solution occurs without contraction) seems to tend to zero with increasing pressure. Here, however, the temperature is not constant, but increases with the pressure.

4. When investigating the fictitious volume change during solution our attention was especially drawn to the system naphthalene-tetrachloroethane<sup>2)</sup>. It seemed to us that this system was extremely suitable for an investigation on the influence of pressure on the solubility. For, in this case, not only  $\Delta v$  is great, but at the same time a very simple method can be applied here for the determination of the composition of saturated solutions. By a pycnometric method the specific volume of these solutions is determined.

In order to determine the solubility curve under pressure, the method followed was a direct one, a modification of the one which we had used previously, when investigating the system *m*-dinitrobenzene-ethylacetate. As the solution of naphthalene in tetrachloroethane assumes a dark colour, when it is in contact with the iron wall of the pressure-bomb, it was necessary to shake the solutions in a glass vessel. When the solution equilibrium had been reached under pressure, the saturated solution under equilibrium-pressure was forced from the glass vessel in the bomb, into some pipettes. From these pipettes the solution, (saturated at  $t^0$  and  $p$  atm.) was pressed into a pycnometer, in order to determine the specific volume

<sup>1)</sup> Physical Review, N.S. 6, 94 (1915).

<sup>2)</sup> Zeitschr. f. physik. Chemie 108, 103 (1924).

of the solution. The concentration could be calculated by means of the equation previously found, which gives the relation between the specific volume and the concentration.

#### *The materials used.*

5. The tetrachlorethane and the naphthalene used in this investigation were prepared and purified in the same way as has previously<sup>1)</sup> been described by us.

#### *Apparatus and Experimental Method.*

6. The shaking bomb (Fig. 2), the thermostat, the piezostat, manometer, and pressure gauge, as well as the thermometers have already previously been described by us<sup>2)</sup>. The shaking bomb was the same that had been used in our investigation on the influence of pressure on the solubility of thallos sulphate; the steel rod *K*, however, had been replaced by a shorter one, in consequence of which there was more space for mercury in the limb *A* of the bomb, so that a greater quantity of liquid could be driven out of the other limb, by pressing oil into *A*.

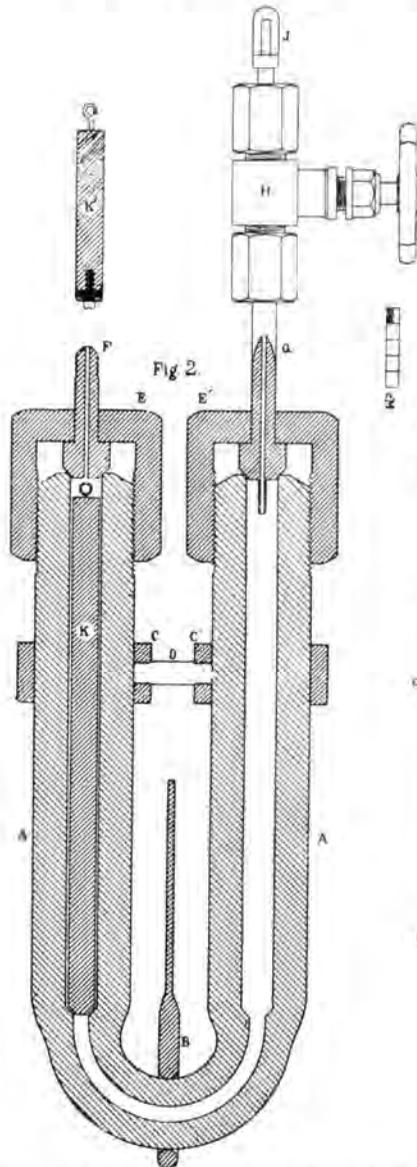
7. The solubility pipette used in this case consisted of a tube *A* (Fig. 3) drawn out at the lower end into a capillary *B*, and provided at the top with a carefully ground stopper *C*, fitting closely on *A*, by means of RAMSAY lubricant. During the shaking of the pipette in the bomb the stopper *A* was kept down by means of two perforated iron plates (*D* and *E*), connected with each other by thin iron wire *G*, *G*, as is shown in the figure. The spiral *F* keeps the wires stretched. During the shaking the capillary *B* is plunged in a glass tube *H*, filled with mercury. The tube is closed with a cork, provided with a slit, through which the mercury of the bomb can pass.

The filling of the pipette, in order to carry out a determination, was done in the following way: The pipette *A* is closed at *B* with a finger. One or two cc. of mercury are put in, and then it is nearly completely filled up with a solution of naphthalene in tetrachlorethane, which, at the pressure at which the investigation will be made, is still unsaturated. Moreover so much solid naphthalene is added, that after reaching the pressure equilibrium "Bodenkörper" is present. The pipette is closed with *C*, so much of the solution is added, that the stopper is also filled with it, and the spiral, the iron plates *D* and *E*, as well as the iron wires are put in place.

<sup>1)</sup> Rec. Trav. Chim. d. Pays-Bas **42**, 779 (1923); Zeitschr. f. physik. Chemie **108**, 103 (1924), especially p. 105.

<sup>2)</sup> Zeitschr. f. physik. Chemie **104**, 323 (1923).

Meanwhile the stopper *E'* (Fig. 2) of the shaking bomb with the cock *H*, has been put upside down between the edges of two tables, and the capillary *G* (*H* is closed) completely filled with mercury.



In the part of the capillary which is now directed upward a plug of cottonwool is inserted, and a piece of thick-walled rubber tube has been shoved over the capillary. This is also filled with mercury and is connected with the glass bulb *K* which is also filled with mercury. The glass bulb enables us to keep the capillary filled with mercury during shaking, and prevents the solution from coming into contact with iron. If this is not carefully seen to, not only impurities will appear in the solution, but at pressures above 750 atm. the solution will be driven out of the tap *H*. When placing the bulb on the india-rubber connexion it must be turned in such a way that, during shaking, when the pipette *A* is pretty well horizontal, the opening *K* of the tube *L* is continually directed upward. Should any of the solution enter the bulb during shaking, it will be left there<sup>1)</sup>, as there is always mercury in the tube *L*, so that the solution can never enter the tap.



When the solution is tapped, — pipette and bulb are now placed in a vertical position —, it can leave the bulb through *K* and *L* unimpeded; the mercury in *G* (Fig. 3) is sometimes driven out as first fraction, sometimes replaced by the solution, and then also sinks into *K*.

In the tube *M* a thick plug of cottonwool is placed, a piece of thick walled rubber tube is shoved over *M* and the pipette *A* is connected

<sup>1)</sup> During shaking the lower half of the bulb, into which *L* opens, will always remain filled with mercury.

with *M*. If the tap with the pipette is now turned 180°, the pipette hangs on the tap. By means of the cork, *B* is placed on the cup *H* filled with mercury. When a certain quantity of mercury has been poured into the limb *A'* of the bomb, the pipette is allowed to sink into this

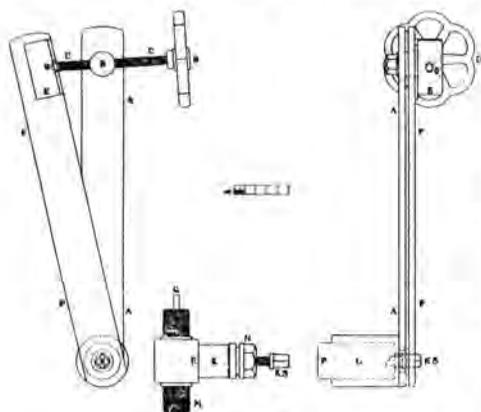


Figure 4.

limb, but care is taken that the mercury stands as high as the upper rim of this leg, before the cap *E'* is screwed on to this limb. In order to get *A'* filled with mercury up to the brim, when the pipette is lowered into this limb, a steel rod *K'* is inserted into the limb *A*, of about one half the length of the rod *K* drawn in the figure. At the bottom this rod is provided with a leather disc. It can move in the limb *A* like a well fitting piston, which drives the mercury into *A'*, and makes it rise in it, until it reaches the brim at the top. The quantity of mercury present in the bomb, must be such that the rod in *A* ends just below the upper rim of *A*. The rest of the remaining space of *A* is filled up with oil. Then *A* is closed with *E*.

8. Now the shaking bomb is lowered into the thermostat, the limb *A* is connected with the pressure capillary, and the motor, which keeps the bomb in motion, is set going.

9. Usually the shaking was continued for eighteen hours, from the afternoon until the following morning. Intensive stirring is due to the mercury which had first been put into the pipette, plus the quantity which enters during the compression of the solution. Moreover the solid naphthalene floats in the solution, so that stirring is not impeded, even when there is a great excess of solid substance.

10. In order to get from the pipette samples of the saturated solution for analysis we proceed as follows: The motor is stopped, the bomb being in a vertical position. After removing the glass cap, which prevented the steel tube *J* from being soiled by oil from the thermostat, a tube of india rubber is shoved over this steel tube *J*. Connected with the india rubber tube is a pipette, the body of which can be closed by two stop-cocks. Then the tap *H* is opened very slowly by means of a key which has been especially constructed for this purpose. Care is taken to keep the pressure in the bomb unchanged, which is done by a supply of oil into the bomb by means of the pressure pump of the piezostat,

which in this case is worked by hand. The special key (see Fig. 4) consists of two levers *A* and *F*, of which *A* is fixed, and *F* can be moved very gradually by means of the wheel *D*, which can turn the screw *CC*, and so opens the tap *K* very slowly.

As it was found that, when tapping, a certain quantity of naphthalene was always deposited — especially at the spot where the transition from high pressure to 1 atm. takes place — and as there was only a rough agreement in the concentrations found of parts of the solution which were tapped consecutively, we have tried to find the cause of this phenomenon. It was found that it is to be attributed to the cooling which manifests itself at the spot where transition from high pressure to 1 atm. takes place. It was proved that naphthalene, carried along mechanically, (the solute in this case is lighter than the saturated solution) was not the cause of this phenomenon, for it showed itself also when the pipette was filled with an unsaturated solution, and solute was present in the shape of small cast bars, sewn in linen bags.

In the concentration of different parts of the tapped, saturated solution a very good agreement was found however, when during tapping a current of warm air blew against the part *H* of the tap. This current was obtained by means of a so called „Fön”, an instrument which is used by hairdressers in drying hair. We connected it up with the electric lighting net (220 Volt), in series with a lamp resistance, so that the current of air had a temperature of 50° C. There was no dissolving of solute during the heating; the plugs of cottonwool prevented the solid naphthalene from rising higher than the bottom of the glass bulb, while the bomb itself is immersed in the oil of the thermostat, almost as far as *H*, during tapping, so that it is not influenced by the warm current of air.

After drawing some cc. of first fraction, we usually tapped the saturated solution consecutively in different pipettes, every time 8 cc.

11. We determined the concentration of these saturated solutions by determining the specific volume at 30°.00 C. In the obliquely drawn out part of the pipette a plug of cottonwool was placed, and this part was connected by means of an india rubber tube with a pycnometer (capacity 6 cc.) according to SPRENGEL-OSTWALD-HOLLEMAN<sup>1)</sup>. To the second stem of this pycnometer a small tube was fixed, and a small bellows to the open end of the pipette. The pycnometer and the pipette are now plunged in a thermostat (30°.00 C.) provided with windows, and both cocks of the pipette are opened, when the whole apparatus has taken on the temperature of the thermostat (after about 15 min.). The saturated solution is pressed slowly into the pycnometer. If it is nearly entirely filled, the tube on the limb of the pycnometer farthest from the pipette

<sup>1)</sup> Rec. Trav. Chim. d. Pays Bas 13, 24 (1894); 19, 79 (1900).

is removed, and this limb is almost quite closed with a finger. If this method of procedure is followed it is impossible that water from the thermostat enters the pycnometer, in consequence of the air escaping from it. As soon as the solution has reached the beginning of the graduation of the limb of the pycnometer, this limb is quite closed with the finger, and the connection of the other limb with the pipette is broken. Then the pycnometer is taken out of the thermostat, and held in such a position, that the solution in both limbs can be read somewhere on the scale.

Now the pycnometer is again immersed in the thermostat, one capillary is quite closed with a finger, and we wait until the apparatus has assumed the temperature of the thermostat, which is seen from the constant position of the meniscus in the open limb.

The pycnometer is now dried and weighed. From the data obtained the specific volume of the saturated solutions is calculated, and their concentration is found by means of the equation (see § 4).

### *Results.*

12. When the preliminary determinations were made, we were led to expect, that it would be possible to continue the measurements up to 1500 atm. The final determinations, however, showed us, that, when at pressures up to 1000 atm. samples of the saturated solutions were tapped in three parts, the agreement in the concentrations of these parts found was very satisfactory, and also when such a test was repeated at the same pressure. This agreement disappeared however at 1250 and 1500 atm. Probably this is to be attributed to the rapid increase over 1000 atm. of the viscosity of the oil which transmits the pressure in the capillary (length 12 M.), which connects the shaking bomb with the piezostat.

An improvement was obtained when lighter oil was used, but the agreement above 1000 atm. was so much worse than the agreement below that pressure, that we shall not consider here the determinations made above 1000 atm.

The great viscosity of the oil causes, when the solution is tapped, a totally different pressure near the tap where the solution flows out, than near the pressure pump, and the manometer indicates the latter pressure.

We hope to construct an apparatus later on, in which the disturbance just mentioned will be eliminated. In this paper we shall consider only such results as have been obtained up to 1000 atm.

Table 1 contains these results.

For computing an interpolation formula which represents the observations we have used the type:

$$c = a + \beta p + \gamma p^2. \quad \dots \quad (1)$$

as well as the form:

$$\log. c = a_1 + \beta_1 p + \gamma_1 p^2 \quad \dots \quad (2)$$

TABLE I.  
 Determinations of solubility in the system Naphtalene-Tetrachlorethane.  
 (Temp. 30°.00 C.).

Number of the Experiment	Pressure in atmospheres	Concentration (in gms. per 100 gms. of solution) of the three tapped parts.			Mean concentration (in gms. per 100 gms. of solution)
1	0	35.07		35.07	35.07
2	250	30.24	30.23	30.25	30.26
3	250	30.29	30.29	30.25	
4	500	26.43	26.41	26.43	26.40
5	500	26.37	26.39	26.39	
6	750	23.34	23.36	23.31	23.33
7	750	23.33	23.30	23.32	
8	1000	20.86	20.92	20.82	20.89
9	1000	20.89	20.89	20.96	

in which  $c$  in both cases represents percentage by weight (solvent = 100, also solution = 100) as well as molecular percentage.

In every case the divergencies between the values found of  $c$  and those computed from the equations, were greater when the equation type 1 was used than with type 2, especially when  $c$  was expressed in percentages of weight of the solvent.

For illustrative purposes we shall in one of the cases also mention the values which were obtained with the equation type 1.

If the concentration is expressed in moles of naphtalene per 100 moles of solution, we find by means of the method of least squares:

$$\log. c = 1.61764 - 0.24196 \cdot 10^{-3} p + 0.03432 \cdot 10^{-6} p^2 \quad . \quad . \quad (a)$$

If we use percentage of weight we find in the same way:

$$\log. c = 1.54504 - 0.26840 \cdot 10^{-3} p + 0.0432 \cdot 10^{-6} p^2 \quad . \quad . \quad (b)$$

and if  $c$  is expressed in percentage of weight (solvent) = 100):

$$\log. c = 1.73224 - 0.39974 \cdot 10^{-3} p + 0.0895 \cdot 10^{-6} p^2 \quad . \quad . \quad (c)$$

and for the other type of equation:

$$c = 53.85 - 44.74 \cdot 10^{-3} p + 17.46 \cdot 10^{-6} p^2 \quad . \quad . \quad . \quad (d)$$

Table 2 gives a survey of the (mean) values found, and of the values calculated by means of the equations (a-d). In the equations (a), (b), and (c) the probable error of a calculated concentration is respectively about 0.03, 0.02, and 0.05 %.

Though the agreement between the values found and those calculated

TABLE 2.  
Determinations of solubility in the system Naphtalene-Tetrachlorethane.  
(Temp. 30°00 C.)

Pressure in atmo- spheres	Mole percentage		Weight perc. $\Sigma=100$		Weight perc. solvent =100		
	found	calc. (a)	found	calc. (b)	found	calc. (c)	calc. (d)
0	41.45	41.46	35.07	35.08	54.01	53.98	53.84
250	36.25	36.25	30.26	30.24	43.39	43.44	43.75
500	31.94	32.01	26.40	26.40	35.87	35.87	35.84
750	28.51	28.54	23.33	23.34	30.43	30.39	30.11
1000	25.71	25.70	20.89	20.89	26.41	26.42	26.58

by means of the equations (a), (b), and (c) is very satisfactory, it again appears how uncertain such equations are when we want to extrapolate. If the pressure is computed, at which a minimum of solubility would appear, the equations (a), (b), and (c) give respectively the values  $p = 3500$ , 3100, and 2200 atm.

So, from the figures found in this case, it would be premature to draw the conclusion that, at increased pressure, the solubility passes through a minimum.

Finally we wish to point out that the system under consideration gives another example of the great influence which pressure can have on solubility. For the first 250 atm. of increase of pressure, the decrease of solubility amounts to about 10.5 % calculated per 100 gms. of solvent. Moreover the divergence from RAOULT's law is, in this case, exactly the opposite of the divergence in the system *m*-dinitrobenzene-ethylacetate. With this system the influence of pressure on solubility was greater than would result from the value  $\Delta v$ . In our case the value of  $\Delta v$ , directly determined <sup>1)</sup>, was 0.1313 cc./gm, whereas the pressure coefficient of solubility for 0 atm. gives  $\Delta v = 0.1082$ , according to the equation:

$$\frac{dl \cdot c}{dp} = -\frac{\Delta v}{RT}$$

which holds good if the solution follows RAOULT's law, in connexion with the equation (a), and with  $R = 82.07$ ,  $T = 303.09$ , l.c. = 2.305 log. c, and the value of the molecular weight of  $C_{10}H_8 = 128.06$ .

While, when RAOULT's law holds good,

$$(1-c) \left( \frac{\partial l \cdot p'}{\partial c} \right)_T = -1$$

<sup>1)</sup> Zeitschr. f. physik. Chem 108, 103 (1924).

(in which  $p'$  represents the vapour pressure of the saturated solution) this factor has now the value of  $-1.21$ . Consequently the vapour pressure of the saturated solution is smaller, the decrease of vapour pressure greater than would be computed from the concentration, when RAOULT'S law holds good.

*Summary.*

The solubility of naphthalene in tetrachlorethane was investigated at  $30^{\circ}.00$  C. and at pressures of 1–1000 atm. A minimum in the solubility curve, which seemed possible on the strength of analogous investigations, could not be established in this system within this interval of pressure.

*Utrecht*, October 1924.

VAN 'T HOFF-*Laboratory.*

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**Chemistry.** — "*On Disaccharins.*" (Second preliminary communication.)  
By H. J. CHOUFOER. (Communicated by Prof. A. F. HOLLEMAN.)

(Communicated at the meeting of December 27, 1924)

*Disaccharins from M-Xylene.*

As was already communicated <sup>1)</sup> through oxidation of 1, 3-xylene, 4,6 disulphanide a product is obtained which melts at 268°—270°. Its N-content was 9,8 %<sub>0</sub>, while 9,7 %<sub>0</sub> is required for a diimide.

No diminution of weight could be observed even on prolonged heating at 140°.

Like WISCHIN I took this product for a disaccharin.

To get more certainty I have tried to titrate this substance. On use of the indicator phenolphthaleine the change of colour is indefinite. Of course carbonic acid free lye and acid were used. For the eq. weight 213 was found. The eq. weight of a diimide is  $\frac{288}{2} = 144$ . When only one of the CH<sub>3</sub>-groups is oxidized, the substance has the eq. weight of 277 or 295 according to whether or no water has been split off. Accordingly my result does not correspond to any of these compounds.

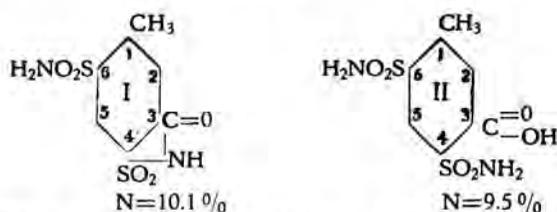
This deviation may be accounted for in different ways. In the first place it may be assumed that a diimide is a very feeble acid. In the second place the possibility exists that the product is a mixture of the said compounds. In the third place it is possible that only one of the CH<sub>3</sub>-groups is oxidized, but that also the SO<sub>2</sub>NH<sub>2</sub>-groups consume part of the lye.

In fact, a good deal of lye appeared to be required to neutralize the disulphanide with respect to phenolphthaleine. The change of colour was very indefinite.

The indicator methylred appeared not to be affected by the diamide. Hence the titration was repeated with methylred as indicator. The colour change was definite. The value of 290 was found for the eq. weight.

It may now be considered as certain that only one of the CH<sub>3</sub>-groups has been oxidized. The product described, which after some crystallisations crystallizes in short, thick, transparent prisms, and possesses the melting-point of 272°, has, therefore, one of the subjoined structures:

<sup>1)</sup> These Proceedings, 27, p. 353.



When  $\text{BaCO}_3$  is added to the solution of this body, it is transformed into the Ba-salt with generation of  $\text{CO}_2$ , which Ba-salt is readily soluble. In this respect it strongly reminds of a sulphonic acid.

Ba weight 19,11 %.

Cal. I 19,83 II 18,84.

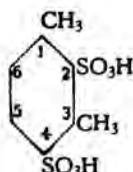
Hence structure II is probably the correct one.

When the diamide is oxidized with the quantity of  $\text{KMnO}_4$  calculated, or rather  $1\frac{1}{3} \times$  the quantity calculated, a precipitate is formed on acidification which consists partly of unchanged diamide, but chiefly of the acid II described above.

If the solution is evaporated after filtration, and when the salt-mass is extracted with alcohol, a hygroscopic mass is left after evaporation of the alcohol. This mass was dissolved in water. The solution gives rise to generation of carbonic acid gas with  $\text{BaCO}_3$ . When the solution is evaporated, a Ba-acid is obtained, which remains viscid even after drying in an exsiccator. If, however, it is boiled out with alcohol, it forms a white powder, which no longer attracts water. It produces no reaction with  $\text{AgNO}_3$  on solution in water, accordingly there is no  $\text{BaCl}_2$  present. A barium determination yielded 23,8 %. The Ba-content is, therefore, considerably higher than of the mono-basic acid. We have possibly here a mixture in which the barium salt of a disaccharin is present.

On further oxidation of the mono-basic acid with  $\text{KMnO}_4$  in aqueous solution, part is recovered unchanged after acidification. In the way described some of the hygroscopic product may be again obtained. In this case the evaporation of the alcohol is followed by a small crystallisation melting at  $112^\circ - 114^\circ$ .

On direct sulphonation of M-xylene there is formed a by-product discovered by PFANNENSTILL, which, as was stated before, probably possesses the structure



To obtain somewhat more of this by-product, I have carried out the sulphonation at higher temperature. Apparently a great quantity of oily disulpho-chloride is then obtained.

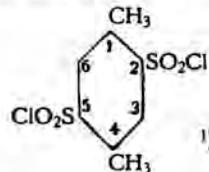
A large part of the 1,3-xylene-4,6-disulpho-chloride, however, remains liquid, in consequence of the formation of resin.

This oil must then be transformed into the amide, and it is very difficult to isolate the diamide from the by-product. After purification the melting-point is 235°. The melting-point of the mixture with 1,3-xylene-4,6 disulphamide presents a deep depression.

After oxidation with  $\text{KMnO}_4$  addition of acid causes only a slight deposition of a precipitate, which appears to be the K-salt of an org. salt. Possibly we may have to do here too with an easily soluble product of oxidation.

#### *Di-saccharins of p-xylene.*

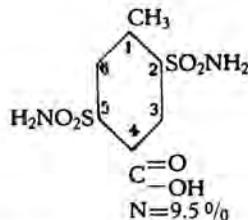
In the direct sulphonation of p-xylene there are formed two di-sulpho chlorides. The by-product possesses a melting-point of 162°, and as I have proved by synthesis, it has the structure:



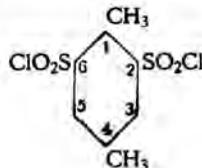
On oxidation the amide prepared from this yielded a product with a melting-point of 320°.

On titration with methyl red as indicator the eq. weight appeared to be 301.3. Here, too, only one methyl group was oxidized.

A whole series of N-determinations gave a mean of 9.4%, which points to the structure



As appears from the following synthesis, the structure of the main product is

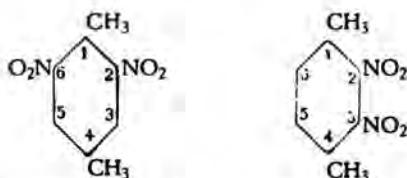


The product started from is p-xylene.

On continued nitration 2 dinitroxylens are formed<sup>2)</sup>, viz.:

<sup>1)</sup> Loc. cit.

<sup>2)</sup> Ber. 19, 144.



which could not be separated by crystallisation in spite of persistent attempts. The mixture was partially reduced by boiling with  $(\text{NH}_4)_2\text{S}$ .

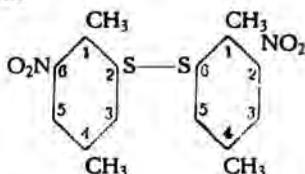
I. It is then converted to a nitroxyldine. Melting-point 96.

II. It becomes a black, tough, resinous mass, insoluble in acid.

On diazotation with  $\text{Na}_2\text{S}_2$  the nitroxyldine from I passes into an orange compound, which admits of filtration, explodes in dry condition and becomes a tough brown mass with aromatic smell.

The orange compound still contains the nitrogen and can be rid of it by being slowly heated on a waterbath stirred with water.

At the ordinary temperature the brown compound is now as hard as stone; it has the structure



as to every grammolecule of nitroxyldine only  $\frac{1}{2}$  gramme molecule of  $\text{Na}_2\text{S}_2$  need to be added.

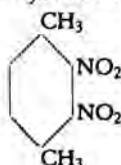
The brown di-sulphide is oxidized by fuming nitric acid with violent generation of heat already at the ordinary temperature. For this reason the more moderate oxidation with nitric acid Sg. 1.4 was preferred. The di-sulphide was, therefore, slowly heated on the water bath with nitric acid. The oxidation takes place near the boiling-point of nitric acid. The substance goes into solution, which is attended with generation of brown  $\text{NO}_2$  vapours. Only a slight quantity of a brown crystallized substance remains behind. When, however, the solution is diluted with water, a larger quantity of a resinous substance is precipitated. Now the solution is distilled off in vacuum. This operation is four times repeated always after addition of water.

Then the distillate no longer reacts acid. The liquid is then neutralized with  $\text{KOH}$ . When the liquid has become slightly alcalic, the colour changes from light yellow to brown. After evaporation of the water the K-salt is changed with  $\text{PCl}_5$  to the sulpho-chloride. When it is poured on ice, a brown solid substance separates. By a few times repeated recrystallisation of this substance from petroleum-ether large pale yellow monoclinic crystals are obtained, which melt at  $61^\circ$ .

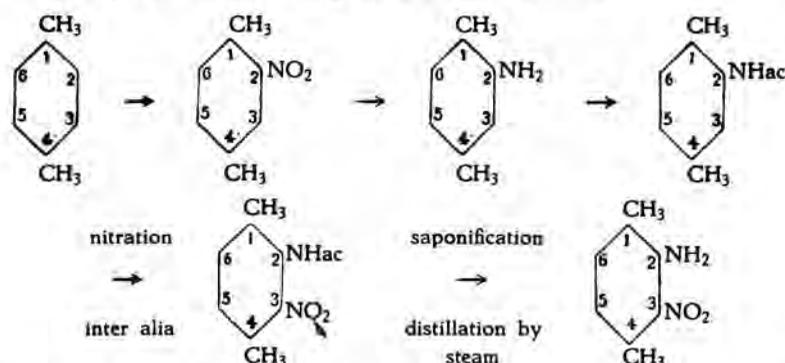
The analysis agrees with the nitrosulphochloride of a xylene. Again the potassium salt of 1,4-xylene-2-nitro-6-sulphonic acid was prepared, but now reduced by boiling with  $(\text{NH}_4)_2\text{S}$ . By means of the diazotation



Evidently this compound does not arise on direct sulphonation of *p*-xylene; it is however, of importance for the synthesis of a disaccharin.

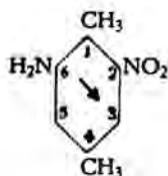
The before mentioned reduction product of  was a resinous

mass, and could not be used as starting-point. In pure condition the nitroxyldine was prepared according to a known method.

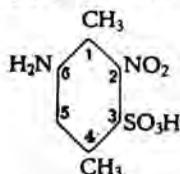


A clear almost colourless oil distilled over, which becomes solid when cooled on ice. This pure compound also appeared to be insoluble in acid, hence unfit for diazotation. Nor is this compound dissolved even by hot nitrous sulphuric acid.

Another possibility of getting the groups at their right places was the sulphonation of



As the  $\text{NH}_2$ -group is strongly *para*-directive, the product expected was:



which by ontamidation would have to be changed into:



Neither at the ordinary temperature, nor at higher temperatures the nitroxylidene was attacked either by fuming sulphuric acid or by chlor-sulphonic acid. On heating with an excess of chlor-sulphonic acid at  $180^{\circ}$  for three hours a considerable carbonisation set in, but part of it was recovered unchanged.

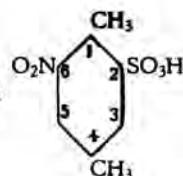
Then followed an investigation of the sulphonation of nitro-xylene. This is dissolved in fuming sulphuric acid, but it is not sulphonized at the ordinary temperature. By prolonged heating at  $110^{\circ}$  there enters a sulpho-group into the nucleus.

The sulphochloride was prepared in the ordinary way. This appeared to be complex, since it presented a melting-range.

By continued fractionated crystallisation from petroleum-ether I succeeded in separating 2 isomer nitro-sulphochlorides, which occur in the mixture in about equal quantities.

1. melting-point  $74.5$
2. " "  $61$ .

The substance melting at  $61^{\circ}$  appeared to be identical with

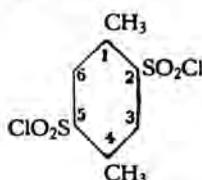


For a further examination the mixture of K-salts was reduced, and changed into the di-sulpho-chlorides by diazotation.

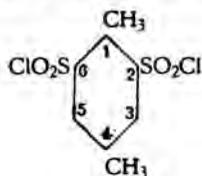
The mixture of di-sulpho-chlorides is liquid. Soon large crystals separate out of the solution in chloroform, melting-point  $157^{\circ}$ .

After recrystallisation the melting-point is  $162^{\circ}$ .

The substance was identical with

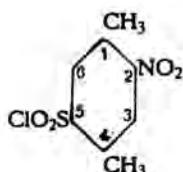


After a few days also needles separate out of the solution in chloroform, melting-point  $72$ . These appeared to be identical with:



Here, too, the quantity of the isomers was about equal.

The first nitro-sulpho-chloride melting-point  $74.5$  has, therefore, the structure:



Finally it remained to study the nitration of P-xylene-sulphonic acid. Para-xylene-sulphonic acid is not attacked by nitric acid sp.gr. 1.4, it is attacked by fuming nitric acid or in sulphuric acid solution with the calculated quantity of nitric acid.

The solution in fuming nitric acid was diluted, and the nitric acid was distilled off in vacuum. The K-salt was changed into the nitro-sulpho-chloride with  $\text{PCl}_5$ . The solution in ether yielded a crystallisation with the melting-point  $107^\circ$  after evaporation of the ether.

A larger quantity of the same substance may be obtained by nitration in sulphuric acid solution with the calculated quantity of  $\text{HNO}_3$ .

It has not yet been decided whether this compound is the still wanting nitro-sulpho-chloride, or possibly a dinitro-sulpho-chloride.

Added after the Dutch proof:

Calc.:	mononitro	N = 5.61 %
	dinitro	N = 9.64 %
Found:		N = 5.62 %

**Physics.** — “Magnetic Resolution of the Scandium Spectrum”. (First Part).<sup>1)</sup> By S. GOUDSMIT, J. VAN DER MARK, and Prof. P. ZEEMAN.

(Communicated at the meeting of December 27, 1924).

*Classification of the lines.*

Several lines of the Scandium spectrum have been arranged into a term system by CATALÁN.<sup>2)</sup> According to him the spectrum of neutral Scandium contains a doublet and a quartet term system, that of ionized Scandium a triplet system. The classification of CATALÁN, however, contains a few inaccuracies, which were evidently also perceived by GIESELER and GROTRIAN<sup>3)</sup> in connection with their observations on the absorption in Scandium. From a theoretical point of view the rectification of the inaccuracies is important.

On account of the particular place which Scandium occupies in the periodic system of the elements — i.e. the first element in this system

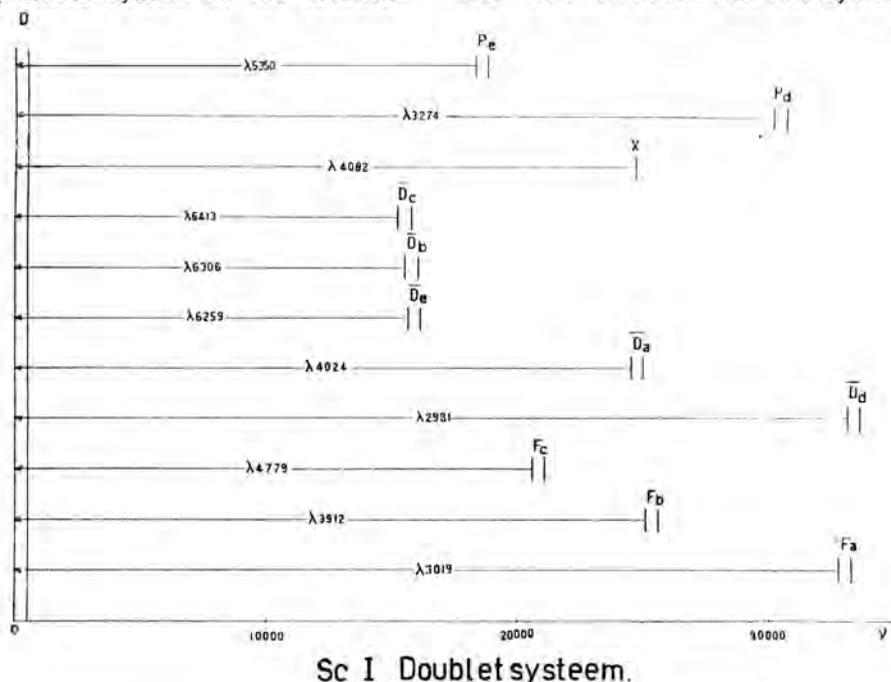


Fig. 1.

<sup>1)</sup> Preliminary communications in Nature, Sept. 20, 1924, Naturw. 12, p. 743, 1924.

<sup>2)</sup> M. A. CATALÁN. An. Soc. Esp. 20, p. 606, 1922, and 21, p. 464, 1923.

<sup>3)</sup> H. GIESELER u. W. GROTRIAN, Zeitschr. f. Phys. 25, p. 342, 1924.

*Note added to the Dutch proof.* In the meantime a publication has appeared by CATALÁN with the corrected term system of ionized Scandium. An. Soc. Esp. 22, p. 497, 1924. Cf. also MEGGERS. Journal of the Washington Academy of Sciences, Vol. 14, N<sup>o</sup>. 18, Nov. 4, 1924.

## Sc I. DOUBLET SYSTEM.

Doublet distance	Relative value of the term	Termsymbol	$J$	$g$
168.5	0	$D_2$	2	$\frac{4}{5}$
	168.5	$D_1$	3	$\frac{6}{5}$
84.1	15672.4	$\overline{D_2^c}$	2	$\frac{4}{5}$
	15756.5	$\overline{D_1^c}$	3	$\frac{6}{5}$
0.8	16021.9	$\overline{D_2^b}$	2	$\frac{4}{5}$
	16022.7	$\overline{D_1^b}$	3	$\frac{6}{5}$
44.0	16096.9	$\overline{D_2^e}$	2	$\frac{4}{5}$
	16140.9	$\overline{D_1^e}$	3	$\frac{6}{5}$
144.6	18711.1	$P_2^e$	1	$\frac{2}{3}$
	18855.7	$P_1^e$	2	$\frac{4}{3}$
53.1	21032.8	$F_2^c$	3	$\frac{6}{7}$
	21085.9	$F_1^c$	4	$\frac{8}{7}$
	24656.7	$X$	—	—
148.0	24866.1	$\overline{D_2^a}$	2	$\frac{4}{5}$
	25014.1	$\overline{D_1^a}$	3	$\frac{6}{5}$
140.1	25584.3	$F_2^b$	3	$\frac{6}{7}$
	25624.4	$F_1^b$	4	$\frac{8}{7}$
133.1	30573.7	$P_2^d$	1	$\frac{2}{3}$
	30706.8	$P_1^d$	2	$\frac{4}{3}$
124.4	33154.1	$F_2^a$	3	$\frac{6}{7}$
	33278.5	$F_1^a$	4	$\frac{8}{7}$
92.3	33614.8	$\overline{D_2^d}$	2	$\frac{4}{5}$
	33707.1	$\overline{D_1^d}$	3	$\frac{6}{5}$

in which completion of an internal group of electrons begins — it seemed of importance to us to confirm the classification of the lines through the examination of the magnetic resolutions, which is the chief end of this investigation.

ARRANGED LINES <sup>1)</sup>. Sc I. DOUBLET SYSTEM.

Arc intensity	$\lambda$ , I. Å.	$\nu_{vac.}$	Combination	Arc intensity	$\lambda$ , I. Å.	$\nu_{vac.}$	Combination
2	2965.88	33707.0	$D_2 \overline{D_1^d}$	3	4753.16	21032.8	$D_2 F_1^c$
3	74.01	614.8	$D_2 \overline{D_2^d}$	3	79.41	20917.3	$D_1 F_1^c$
3	80.75	538.8	$D_1 \overline{D_2^d}$	1	91.56	864.2	$D_1 F_2^c$
2	89.00	446.3	$D_1 \overline{D_2^d}$	1	5301.97	18855.7	$D_2 P_1^c$
3	3015.34	33154.1	$D_2 F_2^a$	1	42.95	711.1	$D_2 P_2^c$
4	19.36	110.0	$D_1 F_1^a$	3	49.70	687.4	$D_1 P_1^c$
2	30.75	32985.6	$D_1 F_2^a$	—	6193.72	16140.9	$D_2 \overline{D_1^c}$
3	3255.67	30706.8	$D_2 P_1^d$	3	6210.68	096.9	$D_2 \overline{D_2^c}$
5	69.84	573.7	$D_2 P_2^d$	2	39.42	022.7	$D_2 \overline{D_1^b}$
5	73.65	538.2	$D_1 P_1^d$	2	39.78	021.8	$D_2 \overline{D_2^b}$
30	3907.54	25584.3	$D_2 F_2^b$	1	58.93	15972.8	$D_1 \overline{D_1^c}$
30	11.88	556.0	$D_1 F_1^b$	1	76.25	928.7	$D_1 \overline{D_2^c}$
6	33.44	415.9	$D_1 F_2^b$	10	6305.72	854.2	$D_1 \overline{D_1^b}$
15	3996.61	25014.1	$D_2 \overline{D_1^a}$	—	06.04	853.4	$D_1 \overline{D_2^b}$
20	4020.40	24866.2	$D_2 \overline{D_2^a}$	1	6344.82	15756.5	$D_2 \overline{D_1^c}$
30	23.68	845.9	$D_1 \overline{D_1^a}$	2	78.80	672.6	$D_2 \overline{D_2^c}$
10	47.81	697.8	$D_1 \overline{D_2^a}$	3	6413.32	588.2	$D_1 \overline{D_1^c}$
10	4054.56	24656.7	$D_2 X$	—	48.20	503.9	$D_1 \overline{D_2^c}$
15	82.44	488.3	$D_1 X$				

<sup>1)</sup> Wave-lengths and intensities according to EXNER and HASCHEK, corrected to I. Å.  
9\*

## Sc II. TRIPLET SYSTEM.

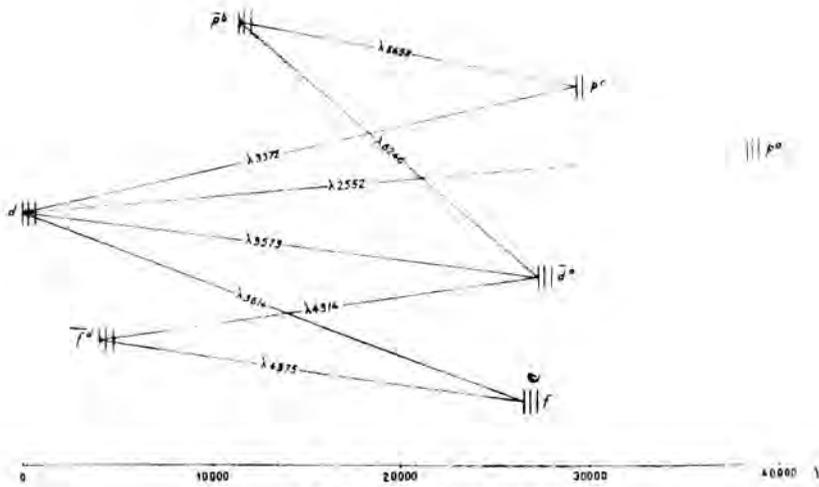
Triplet distance	Relative value of the term	Termsymbol	$J$	$g$
	0	$d^3$	$1\frac{1}{2}$	$\frac{1}{2}$
67.6	67.6	$d_2$	$2\frac{1}{2}$	$\frac{7}{6}$
110.2	177.8	$d_1$	$3\frac{1}{2}$	$\frac{4}{3}$
	4802.4	$\overline{f}_3^d$	$2\frac{1}{2}$	$\frac{2}{3}$
80.8	4883.2	$\overline{f}_2^d$	$3\frac{1}{2}$	$\frac{13}{12}$
104.3	4987.5	$\overline{f}_1^d$	$4\frac{1}{2}$	$\frac{5}{4}$
	12073.8	$\overline{p}_3^b$	$\frac{1}{2}$	$0/0$
27.5	12101.3	$\overline{p}_2^b$	$1\frac{1}{2}$	$\frac{3}{2}$
52.8	12154.1	$\overline{p}_1^b$	$2\frac{1}{2}$	$\frac{3}{2}$
	27443.9	$f_3$	$2\frac{1}{2}$	$\frac{2}{3}$
158.8	27602.7	$f_2$	$3\frac{1}{2}$	$\frac{13}{12}$
238.7	27841.4	$f_1$	$4\frac{1}{2}$	$\frac{5}{4}$
	27918.1	$\overline{d}_3^e$	$1\frac{1}{2}$	$\frac{1}{2}$
103.5	28021.6	$\overline{d}_2^e$	$2\frac{1}{2}$	$\frac{7}{6}$
139.4	28161.5	$\overline{d}_1^e$	$3\frac{1}{2}$	$\frac{4}{3}$
	29742.3	$p_2^c$	$1\frac{1}{2}$	—
81.9	29824.2	$p_1^c$	$2\frac{1}{2}$	$\frac{3}{2}$
	39002	$p_3^a$	$\frac{1}{2}$	$0/0$
113	39115	$p_2^a$	$1\frac{1}{2}$	$\frac{3}{2}$
231	39346	$p_1^a$	$2\frac{1}{2}$	$\frac{3}{2}$

Here follows first of all the corrected term scheme for the doublet and the triplet system.

The term  $d_3$ , which was put equal to 0 here, very probably belongs

## ARRANGED LINES. Sc II. TRIPLET SYSTEM.

Spark intensity	$\lambda$ , I, Å.	$\nu_{vac}$ .	Combination	Spark intensity	$\lambda$ , I, Å.	$\nu_{vac}$ .	Combination
—	2540.86	39345.0	$d_3 p_1^a$	1	4279.93	23358.3	$\overline{f_3^d} \overline{d_1^a}$
4	45.19	278.1	$d_2 p_1^a$	5	94.78	277.6	$\overline{f_2^d} \overline{d_1^a}$
8	52.39	167.2	$d_1 p_1^a$	6	4305.72	218.4	$\overline{f_3^d} \overline{d_2^a}$
4	55.82	114.6	$d_3 p_2^a$	30	14.09	173.4	$\overline{f_1^d} \overline{d_1^a}$
6	60.28	046.5	$d_2 p_2^a$	20	20.75	137.7	$\overline{f_2^d} \overline{d_2^a}$
4	63.21	002.0	$d_3 p_3^a$	20	24.99	115.0	$\overline{f_3^d} \overline{d_3^a}$
2	3352.05	29824.5	$d_3 p_1^c$	5	4354.61	22957.7	$\overline{f_2^d} f_1$
8	59.69	756.6	$d_2 p_1^c$	30	74.51	853.3	$\overline{f_1^d} f_1$
8	61.31	742.3	$d_3 p_2^c$	5	84.80	799.7	$\overline{f_3^d} f_2$
10	68.96	674.7	$d_2 p_2^c$	20	4400.39	718.9	$\overline{f_2^d} f_2$
10	72.16	646.4	$d_1 p_1^c$	20	15.55	640.9	$\overline{f_3^d} f_3$
20	3558.56	28093.3	$d_2 \overline{d_1^a}$	2	20.66	614.7	$\overline{f_1^d} f_2$
20	67.72	021.1	$d_3 \overline{d_2^a}$	3	31.36	560.1	$\overline{f_2^d} f_3$
50	72.57	27983.1	$d_1 \overline{d_1^a}$	1	5641.00	17722.5	$\overline{p_2^b} p_1^c$
30	76.37	953.3	$d_2 \overline{d_2^a}$	2	57.89	669.5	$\overline{p_1^b} p_1^c$
20	80.98	917.4	$d_3 \overline{d_3^a}$	1	58.35	668.1	$\overline{p_3^b} p_2^c$
10	89.67	849.8	$d_2 \overline{d_3^a}$	1	67.19	640.5	$\overline{p_2^b} p_2^c$
10	90.52	843.2	$d_1 \overline{d_2^a}$	1	84.22	587.7	$\overline{p_1^b} p_2^c$
100	3613.83	27663.6	$d_1 f_1$	1	6245.64	16006.8	$\overline{p_1^b} \overline{d_1^a}$
100	30.75	534.7	$d_2 f_2$	1	79.74	15919.8	$\overline{p_2^b} \overline{d_2^a}$
50	42.96	443.6	$d_3 f_3$	—	6300.64	867.0	$\overline{p_1^b} \overline{d_2^a}$
15	45.48	424.6	$d_1 f_2$	1	09.94	843.6	$\overline{p_3^b} \overline{d_3^a}$
20	51.99	375.7	$d_2 f_3$	—	20.85	816.3	$\overline{p_2^b} \overline{d_3^a}$
3	66.68	266.0	$d_1 f_3$	—	42.02	763.5	$\overline{p_1^b} \overline{d_3^a}$



Sc II Triplet system.

Fig. 2.

to the lowest of the levels of energy discussed here. Whether it is also the lowest possible level of ionized Scandium cannot be decided as yet.

#### *Experimental part.*

In the investigation a concave Rowland grating was used as spectrograph, mounted in the way indicated by EAGLE<sup>1)</sup>. The grating has 14438 lines to the inch; width 5 inches (originally 6 inches), a strip of 1 inch on one of the sides of the grating gave rise to disturbances, and was therefore covered when the photo was taken; radius of curvature 21 feet.

The photos were taken in the 2<sup>nd</sup> order on plates 50 cm. long, which covered an area of about 600 Å, so that the dispersion amounted to about 1,2 Å per mm. The drawback of the EAGLE mounting is that the photographic focussing must be made anew for every area. As source of light a MERTON vacuum iron arc lamp appeared to be very efficient<sup>2)</sup>. With the ordinary iron arc in air the very delicate adjustment necessary for the photographing of the resolution figures, was much more difficult to attain on account of the lines being less fine.

The brightness of the grating is rather small, so that exposures of 5 hours appeared to be necessary.

The magnetic field was produced by a Weiss-magnet with water cooling which gave a field of about 41000 Gauss with the distance of the poles used and with a current of 100 Ampères. The current was supplied by a converter, with which the strength of the current could be kept sufficiently constant. The cooling of the magnet was very efficient, so much so that its temperature was lower than that of the room.

<sup>1)</sup> Astroph. Journ. 31, p. 120, 1910.

<sup>2)</sup> Prof. MERTON was so kind as to put a drawing of his lamp at the disposal of one of us (P. Z.).

As source of light in the field a vacuum trembler was used, a modification of BACK'S Abreissbogen <sup>1)</sup>. The modification consists in this that the mechanical arrangement that works the tungsten electrode in BACK'S experiment, has been discarded, and that the current itself works it. The arrangement is briefly this <sup>2)</sup>: the tungsten electrode is fastened to a pendulum, which can move freely in the direction from pole to pole. By means of a feeble spring with a tension adjustable from the outside, the tungsten electrode is always pressed against the other, fixed electrode.

The whole apparatus is made so small that it can be contained inside the vacuum pot which is placed between the pole pieces, and fastened, like the other electrode, to a ground-in metal stopper, so as to render quick removal possible. Now the current must pass through a solenoid which is fastened to the pendulum, and the axis of which is at right angles to the direction of the lines of force between the polar pieces of the magnet. The solenoid is still in a very strong field, so that it need have only few turns to draw the tungsten electrode from the other and produce an interrupting spark or arc, if the current direction be chosen well.

The spark burned in hydrogen of low pressure, just as in BACK'S arrangement. We, however, admitted hydrogen through a narrow capillary, which was sucked off again by a slowly running Gaede pump, so that we experienced less trouble of small leakages, which are sometimes inevitable.

Scandium being unknown in metallic state, it was not possible to use a metal electrode for the spark. We were, therefore, obliged to have recourse to carbon electrodes. Carbon pieces, sawn out of arc-lamp carbon, appeared too much liable to breakage, on account of the required small dimensions (about  $20 \times 1 \times 1.5$  mm.), and they contained too many contaminations. This induced us to make the carbon pieces ourselves. The material for them is soot, obtained from a smoking kerosene flame. This is mixed with anhydrous coal tar, kneaded, and at last beaten till a very stiff paste is obtained. By the aid of a very simple compressing cylinder with piston placed in a bench vice, this paste is spouted to a long thread with the required rectangular cross-section. This thread is cut to pieces of the desired length. The carbon pieces, which are still soft, are carefully packed in a crucible with graphite, and kept yellow-red hot for three quarters of an hour. After the outer crust of graphite had been ground off, strong metallic-sounding carbon pieces were obtained, which hardly ever broke.

Carbons, into which Scandium oxide had already been entered during the preparation, appeared to give only a feeble spectrum. Carbon soaked in the chloride, appeared to give a better result. In order to introduce as much Scandium into the carbons as possible, the carbons were first kept

<sup>1)</sup> Ann. d. Phys. Bd. 70, 1923, p. 336.

<sup>2)</sup> A more detailed description will follow.

under vacuum for a long time, then a concentrated Scandium solution was admitted, after which the vacuum was broken. The carbons obtained in this way, contained only very weak contaminations, chiefly calcium.

The application of carbons in the vacuum trembler has a drawback, viz. that the tungsten electrode is pretty quickly consumed. This is the reason that we do not apply as BACK a ground tungsten electrode of a definite shape, but an ordinary tungsten filament (thickness 0,6 mm.) which can be easily replaced. The carbons themselves are only very slowly consumed, one carbon is sufficient for four hours' illumination.

The plates have been measured in four different ways;

1. with the comparator,
2. with the micro-photometer,
3. in the projected image.

For sharp lines of a certain degree of blackness the comparator appeared the most suitable method, the micro-photometer gave the best results for diffuse lines (pseudo-triplets and similar lines), the last method appearing to be the best for exceedingly weak lines. An image of the lines was thrown on a screen with a known magnification by micro-projection, and then measured. Very feeble lines for which the adjustment could not be made accurately in the comparator, and which could not be seen in consequence of the grain in the micro-photogram, could still be measured very well by this method. In the measurement of very diffuse lines the adjustment was made for the centre of gravity of the blackening; for some of these lines it was also still possible to make the adjustment for the sharp boundary line of the components, which measurement was then in good agreement with theory.

Measurements were made in the regions of 3900—4500 Å, and 3200—3900 Å. Other regions will follow. At the moment a new, much brighter grating arrangement is being constructed in the laboratory, which will be taken in use very soon. With this apparatus some other parts of the spectrum will be examined, besides other lines, which are still doubtful. Between 3900—4500 Å the normal triplet distance has been calculated from the resolutions of the calcium triplet  $\lambda$  4226 and the calcium quadruplet  $\lambda$  3968. The calcium sextet  $\lambda$  3933 also occurs on the photographic plates; at some tenths of Å there occurs a very feeble Scandium line, which all the same deforms the sextet perceptibly.

Starting from the region of 3200 Å there did not occur a single foreign line suitable for a determination of the intensity of the field. From the photographs in the preceding region it had, however, already been ascertained, what resolutions the Scandium lines  $\lambda\lambda$  3572, 3576, and 3581 would have to present. These lines give all three sharp triplets. We have used these lines for the determination of the intensity of the field. This appears to be justified on account of the good agreement presented by the resolutions of the other Scandium lines with the resolutions predicted.

We have, therefore, omitted to take a special photograph for the determination of the field intensity.

On the whole the Scandium lines, even the sharp triplets, are somewhat diffuse. Consequently the attainable accuracy is not very great. It is, of course, also different for different lines. As a general datum for the accuracy of the measurements it may be stated that the position of the components could be determined up to an average of  $0.006 \text{ \AA}$ . For sharp lines the mean deviation from the mean value was  $0.0025 \text{ mm.} = 0.0033 \text{ \AA}$  for a series of 10 observations, it increased to  $0.008 \text{ mm.} = 0.010 \text{ \AA}$  for very hazy lines. When it is also stated that the widest resolution was  $\pm 0.66 \text{ \AA}$  from central to outer component, and the narrowest  $\pm 0.12 \text{ \AA}$ , it appears that the error which will be finally present in the result, can never be very small.

#### THE MAGNETIC RESOLUTIONS.

##### *Sc I Doublet system.*

##### Combinations *DD*

$\lambda$ 3996.61	$D_2 \bar{D}_1^a$	$J=2, g = \frac{4}{5}$ with $J=3, g = \frac{6}{5}$
		type $\frac{(13)579}{5}$
observed	1.79 1.40 1.00 (0.62) (0.19) (0.19) (0.56) 0.98 1.40 1.76	
calculated	1.80 1.40 1.00 (0.60) (0.20) (0.20) (0.60) 1.00 1.40 1.80	

$\lambda$ 4020.40	$D_2 \bar{D}_2^a$	$J=2, g = \frac{4}{5}$ with $J=3, g = \frac{4}{5}$
		type $\frac{(0)4}{5}$
observed	0.80 (0) 0.81	sharp
calculated	0.80 (0) 0.80	sharp

$\lambda$ 4023.68	$D_1 \bar{D}_1^a$	$J=3, g = \frac{6}{5}$ with $J=3, g = \frac{6}{5}$
		type $\frac{(0)6}{5}$ Fig. 3
observed	1.21 (0) 1.21	sharp
calculated	1.20 (0) 1.20	sharp

$\lambda$ 4047.81	$D_1 \bar{D}_2^a$	$J=3, g = \frac{6}{5}$ with $J=2, g = \frac{4}{5}$
		type $\frac{(13)579}{5}$
observed	1.77 1.39 0.98 (0.59) (0.19) (0.19) (0.56) 0.96 1.33 1.71	
calculated	1.80 1.40 1.00 (0.60) (0.20) (0.20) (0.60) 1.00 1.40 1.80	

The observed resolution of this group fully agrees with the calculations.

This confirms, therefore, that we have really to do here with a doublet *DD*-group. The asymmetries are real.

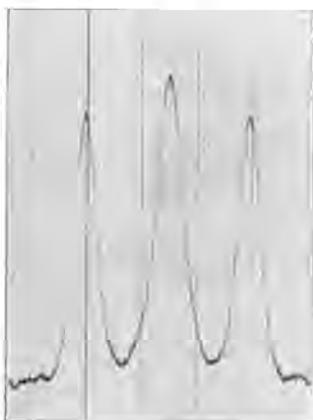


Fig. 3.  $\lambda$  4023.68.

Accordingly these resolutions also confirm GIESELER and GROTRIAN's <sup>1)</sup> view that the fundamental term of *ScI* is a doublet *D*-term; for according to their absorption experiments it is the term  $D_2$  put equal to 0 in our term system.

According to BOHR and COSTER <sup>2)</sup> the neutral Scandium atom must contain one  $3_3$ - and two  $4_1$ -electrons. If during the emission this  $3_3$ -electron were still present in the atom rest, so-called terms "höherer Stufe" with entirely new resolutions would have to be expected according to LANDÉ <sup>3)</sup>. As this is very certainly not the case, their  $3_3$ -electron must necessarily be the emitting electron. This is also in harmony with STONER's <sup>4)</sup> electron system, according to which the fundamental term must then have the symbol  $3_{32}$ . For the fundamental path *J* is actually = 2.

Except under special circumstances the splitting up of the group furnishes already an important support for the accuracy of the other term symbols. For from the way in which the other terms combine with the known *D*-fundamental term, it is possible to determine their quanta-values *J*, hence to establish the term symbol with pretty great certainty.

Further the following lines were split up:

$\lambda$ 3907.54	$D_2 F_2^b$	$J=2, g = 1/5$ with $J=3, g = 6/7$
	type	$\frac{(1\ 3)\ 27\ 29\ 31\ 33}{35}$
	observed	0.90 (0) 0.91 pretty sharp
	calculated	< 0.94 (0) < 0.94 pretty sharp
$\lambda$ 3911.88	$D_1 F_1^b$	$J=3, g = 6/5$ with $J=4, g = 8/7$
	type	$\frac{(1\ 35)\ 35\ 37\ 39\ 41\ 43\ 45}{35}$
	observed	1.07 (0) 1.06 sharp inside
	calculated	> 1.00 (0) > 1.00 sharp inside

<sup>1)</sup> loc. cit.

<sup>2)</sup> N. BOHR and D. COSTER, Zeitschr. f. Phys. 12, p. 342, 1923.

<sup>3)</sup> A. LANDÉ, Zeitschr. f. Phys., 17, p. 292, 1923.

<sup>4)</sup> E. C. STONER, Phil. Mag. 48, 719, 1924.

$\lambda$ 3269.84	$D_2 P_2^d$	$J=2$	$g = 1/5$	with	$J=1$	$g = 2/3$	
		type		$\frac{(1) 11 13}{15}$			
observed	0.87	(0)		0.76	feeble, vague		
calculated	0.86	0.74	(0.07)	(0.07)	0.74	0.86	

*Sc II Triplet system.*

Combinations $dd$							
$\lambda$ 3558.56	$d_2 \bar{d}_1^a$	$J=2\frac{1}{2}$	$g = 7/6$	with	$J=3\frac{1}{2}$	$g = 4/3$	
		type		$\frac{(0) 1 2) 6 7 8 9 10}{6}$			
observed	1.63	(0)	1.64	sharp	outside		
calculated	< 1.67	(0)	< 1.67	sharp	outside		
$\lambda$ 3567.72	$d_3 \bar{d}_2^a$	$J=1\frac{1}{2}$	$g = 1/2$	with	$J=2\frac{1}{2}$	$g = 7/6$	
		type		$\frac{(0) 3 (4) 7 11}{6}$			
observed	1.83	1.16	0.64	(0)	0.64	1.15	1.82
calculated	1.83	1.17	$\widetilde{(0.67)}$	0.50	(0)	$\widetilde{0.50}$	$\widetilde{(0.67)}$

The measurement was made on a plate on which the two polarisation states had been photographed at the same time. In consequence of this the stronger  $\pi$  component (0.67) had combined with the weak  $\sigma$  component 0.50. Fig. 4.

$\lambda$ 3572.57	$d_1 \bar{d}_1^a$	$J=3\frac{1}{2}$	$g = 4/3$	with	$J=3\frac{1}{2}$	$g = 4/3$	
		type		$\frac{(0) 4}{3}$			
observed	1.31	(0)	1.34	sharp			
calculated	1.33	(0)	1.33	sharp			
$\lambda$ 3576.37	$d_2 \bar{d}_2^a$	$J=2\frac{1}{2}$	$g = 7/6$	with	$J=2\frac{1}{2}$	$g = 7/6$	
		type		$\frac{(0) 7}{6}$			
observed	1.14	(0)	1.19	sharp			
calculated	1.17	(0)	1.17	sharp			
$\lambda$ 3580.98	$d_3 \bar{d}_3^a$	$J=1\frac{1}{2}$	$g = 1\frac{1}{2}$	with	$J=1\frac{1}{2}$	$g = \frac{1}{2}$	
		type		$\frac{(0) 1}{2}$			
observed	0.51	(0)	0.51	sharp			
calculated	0.50	(0)	0.50	sharp			
$\lambda$ 3589.67	$d_2 \bar{d}_3^a$	$J=2\frac{1}{2}$	$g = 7/6$	with	$J=1\frac{1}{2}$	$g = 1/2$	
		type		$\frac{(0) 3 (4) 7 11}{6}$			

observed	<b>1.83</b>	1.17	<u>0.65</u>	(0)	<u>0.61</u>	1.18	[1.76]
calculated	<b>1.83</b>	1.17	(0.67)	0.50	(0)	0.50	(0.67) 1.17 <b>1.83</b>

Compare remark to  $\lambda$  3567.72. The component [1.76] coincides with the component [1.42] of the following line. Fig. 5.

$\lambda$  **3590.52**  $d_1 \bar{d}_2^a$   $J = 3\frac{1}{2}, g = \frac{4}{3}$  with  $J = 2\frac{1}{2}, g = \frac{7}{6}$

type  $\frac{(0\ 1\ 2)\ 6\ 7\ 8\ 9\ 10}{6}$

observed	[1.42]	(0)	1.51	sharp outside
calculated	< 1.67	(0)	< 1.67	sharp outside

Splitting up too simple, comp.  $\lambda$  3558.56.



Fig. 4.  $\lambda$  3567.62

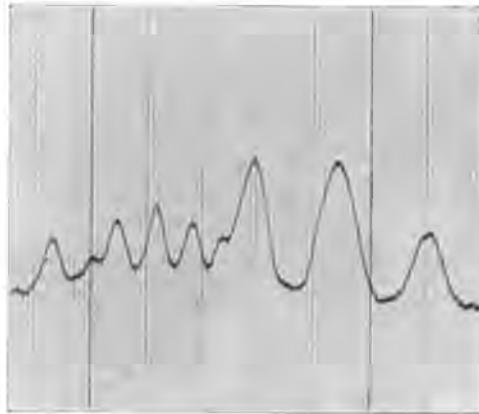


Fig. 5.  $\lambda$  3589.67 and  $\lambda$  3590.72.

Combinations  $df$ .

$\lambda$  **3613.83**  $d_1 f_1$   $J = 3\frac{1}{2}, g = \frac{4}{3}$  with  $J = 4\frac{1}{2}, g = \frac{5}{4}$

type  $\frac{(0\ 1\ 2\ 3)\ 12\ 13\ 14\ 15\ 16\ 17\ 18}{12}$

observed	1.11	(0)	1.12	sharp inside
calculated	> 1.00	(0)	> 1.00	sharp inside

$\lambda$  **3630.75**  $d_2 f_2$   $J = 2\frac{1}{2}, g = \frac{7}{6}$  with  $J = 3\frac{1}{2}, g = \frac{13}{12}$

type  $\frac{(0\ 12\ 3)\ 11\ 12\ 13\ 14\ 15\ 16}{12}$

observed	1.03	(0)	1.03	sharp inside
calculated	> 0.92	(0)	> 0.92	sharp inside

Splitting up too great comp.  $\lambda$  4320.75.

$\lambda$  **3642.96**  $d_3 f_3$   $J = 1\frac{1}{2}, g = \frac{1}{2}$  with  $J = 2\frac{1}{2}, g = \frac{2}{3}$

type  $\frac{(0\ 1)\ 3\ 4\ 5}{6}$

observed	0.78	(0)	0.79	very broad
calculated	< 0.83	(0)	< 0.83	sharp outside

$\lambda$  3645.48  $d_1 f_2$   $J = 3\frac{1}{2}, g = \frac{1}{3}$  with  $J = 3\frac{1}{2}, g = \frac{13}{12}$   
 type  $\frac{(3\ 6\ 9)\ 7\ 10\ 13\ 16\ 19\ 22}{12}$

observed ? 0.69 0.68 ?  $\perp$  very vague  
 calculated 1.21  $< (0.75) < (0.75)$  1.21  $\perp$  not sharp

$\lambda$  3651.99  $d_2 f_3$   $J = 2\frac{1}{2}, g = \frac{7}{6}$  with  $J = 2\frac{1}{2}, g = \frac{2}{3}$   
 type  $\frac{1\ (3)\ 4\ (6)\ 7\ 10}{6}$

observed 1.58 1.00 0.57 0.57 1.04 1.67  
 calculated 1.67  $\overline{1.17}$   $\overline{(1.00)}$   $\overline{0.67}$   $\overline{(0.50)}$  0.16 0.16  $\overline{(0.50)}$   $\overline{0.67}$   $\overline{(1.00)}$   $\overline{1.17}$  1.67

Cf. remark to  $\lambda$  3567.72. Asymmetric, inner components too weak.

$\lambda$  4314.09  $\bar{f}_1 \bar{d}_1^a$   $J = 4\frac{1}{2}, g = \frac{5}{4}$  with  $J = 3\frac{1}{2}, g = \frac{1}{3}$   
 type  $\frac{(0\ 1\ 2\ 3)\ 12\ 13\ 14\ 15\ 16\ 17\ 18}{12}$

observed 1.09 (0) 1.10 sharp inside  
 calculated  $> 1.00$  (0)  $> 1.00$  sharp inside

$\lambda$  4320.75  $\bar{f}_1 \bar{d}_2^a$   $J = 3\frac{1}{2}, g = \frac{13}{12}$  with  $J = 2\frac{1}{2}, g = \frac{7}{6}$   
 type  $\frac{(0\ 1\ 2\ 3)\ 11\ 12\ 13\ 14\ 15\ 16}{12}$

observed 0.98 (0) 0.96 sharp inside  
 calculated  $> 0.92$  (0)  $> 0.92$  sharp inside

$\lambda$  4325.00  $\bar{f}_3 \bar{d}_3^a$   $J = 2\frac{1}{2}, g = \frac{2}{3}$  with  $J = 1\frac{1}{2}, g = \frac{1}{2}$   
 type  $\frac{(0\ 1)\ 3\ 4\ 5}{6}$

observed 0.79 (0) 0.79 sharp outside  
 calculated  $< 0.83$  (0)  $< 0.83$  sharp outside

Combinations  $f f$ .

$\lambda$  4374.51  $\bar{f}_1^a f_1$   $J = 4\frac{1}{2}, g = \frac{5}{4}$  with  $J = 4\frac{1}{2}, g = \frac{5}{4}$   
 type  $\frac{(0)\ 5}{4}$

observed 1.28 (0) 1.37 sharp  
 calculated 1.25 (0) 1.25 sharp

$\lambda$  4400.39  $\bar{f}_2^a f_2$   $J = 3\frac{1}{2}, g = \frac{13}{12}$  with  $J = 3\frac{1}{2}, g = \frac{13}{12}$   
 type  $\frac{(0)\ 13}{12}$

observed 1.09 (0) 1.10 sharp  
 calculated 1.08 (0) 1.08 sharp

$\lambda$ 4415.55	$\bar{f}_1^d f_1$	$J = 2\frac{1}{2}, g = \frac{2}{3}$ with $J = 2\frac{1}{2}, g = \frac{2}{3}$		
		type $\frac{(0) 2}{3}$		
observed	0.69	(0)	0.67	sharp
calculated	0.67	(0)	0.67	sharp
Combinations $dp$ .				
$\lambda$ 3372.16	$d_1 p_1^c$	$J = 3\frac{1}{2}, g = \frac{4}{3}$ with $J = 2\frac{1}{2}, g = \frac{3}{2}$		
		type $\frac{(0 12) 6 7 8 9 10}{6}$		
observed	1.16	(0)	1.13	sharp inside
calculated	> 1.00	(0)	> 1.00	sharp inside
$\lambda$ 3359.69	$d_2 p_1^c$	$J = 2\frac{1}{2}, g = \frac{7}{6}$ with $J = 2\frac{1}{2}, g = \frac{3}{2}$		
		type $\frac{(2 4) 5 7 9 11}{6}$		
observed	?	0.66	0.66	? very vague
calculated	1.33 <	(0.67) <	(0.67)	1.33 $\perp$ broad, not sharp
Unclassified lines.				
$\lambda$ 3353.74				
observed	1.00	(0)	1.00	not sharp
$\lambda$ 3535.74				
observed	0.98	(0)	1.02	sharp
$\lambda$ 4246.88				
observed	0.99	(0)	0.98	pretty sharp

Accordingly these lines, which give normal triplets, probably belong to the simple term system of ionized Scandium.

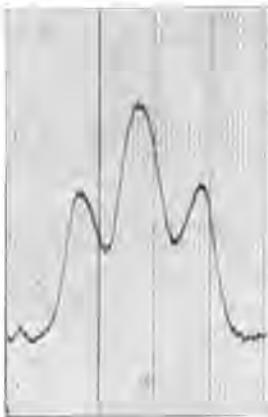


Fig. 6.  $\lambda$  4325.00.

It may be pointed out here that splitting-up types, which in  $sp$ -combinations are still easily resolvable, can no longer be resolved in  $dd$ -,  $df$ - and other combinations, as also the original lines are generally much less sharp.

The investigation of some important lines is still in progress. These are first of all the  $ScI$ -lines  $\lambda$  4054.56 and  $\lambda$  4082.44. The intensity of these lines greatly decreases in the magnetic field, so that it was not yet possible to measure out the resolutions. Preliminary observations render it, however, probable that the effect met with here is the partial Paschen-Back effect, so that the term denoted by  $X$  in the term system is probably a doublet  $P$ ,  $D$  or  $F$  term that has coincided.

More or less the same thing seems to be the case with the triplet term  $p^c$ . Probably *two* terms of this,  $p_2^c$  and  $p_3^c$ , seem to have almost coincided. The fuller examination of the resolution of the lines  $\lambda$  3368 and  $\lambda$  3361 must still confirm this.

The correctness of the classification of the lines of ionized Scandium appears from the resolutions given above. So far no terms "höherer Stufe" were found in this either. We may, therefore, refer to the recently analyzed spectrum of the allied ionized Lanthanum <sup>1)</sup>. From earlier measurements of the magnetic resolution <sup>2)</sup> it appeared with certainty that there occur a number of these terms "höherer Stufe" in this spectrum. Possibly these are found only in feeble lines in the Scandium spectrum.

In conclusion we may express our cordial thanks to Messrs. Prof. BOHUSLAV BRAUNER, and Prof. ŠTĚRRA—BÖHM at Prague, who enabled us to carry out this investigation, by supplying us with perfectly pure  $\text{Sc}_2\text{O}_3$ .

*Amsterdam, December 1924.*

*Laboratory "Physica".*

<sup>1)</sup> S. GOUDSMIT, These Proceedings 28 p. 23, Naturw. 12, p. 851, 1924.

<sup>2)</sup> S. RYBAR, Phys. Zeitschr. 12, p. 889, 1911.

**Astronomy.** — "*The Light-Curve of the Cepheids*". By Prof. A. A. NIJLAND.

(Communicated at the meeting of January 31, 1925).

It has been tried to establish a connection between the Cepheids and the semi-regular long-period variable stars of the Mira-type. In fact, in some respects the mean curve of the Cepheids may be considered as a reduced copy of that of the long-period variables, assuming for a moment, that there can be question of mean curves for phenomena each presenting so much variety. If for the mean periods of Cepheids and long-period variables  $6^d$  and  $300^d$  is taken, respectively, a proportion of 50 is found, which presents itself also in the range of the light variation, at least when magnitudes are converted into light-intensities. For the ratio 50 corresponds to a difference of  $4\frac{1}{4}$  magnitudes; and, as a matter of fact, this is about what observation has taught about the difference of range of the mean light-variation of Cepheids ( $1^m$ ) and long-period variables ( $5^m$ ). It is to be remarked, however, that the light-intensity curve of the Mira-variables resembles more closely that of e.g.  $V 18 = RZ \textit{Camelopardalis}$  or  $V 18 = RZ \textit{Lyrae}$  <sup>1)</sup> than that of  $\delta \textit{Cephei}$ .

It is interesting to ascertain whether the asserted analogy goes still further. The semi-regular variables of the Mira-type exhibit irregularities both in period and in amplitude. Moreover the light-curves have every now and then secondary undulations or humps, which often attain a full magnitude, and can be proved to exist beyond any doubt. No unanimity has been reached on the question whether this is the case in the same degree also with the Cepheids. It will be readily admitted that without doubt all these irregularities will occur here too *occasionally*. The secondary wave with  $S \textit{Sagittae}$  is incontestable, and the case of  $\eta \textit{Aquilae}$  <sup>2)</sup>, which is perfectly confirmed by simultaneous Utrecht observations <sup>3)</sup>, speaks for itself. Whether, however, the changes, which according to some astronomers are supposed to continually modify the light-curve of e.g.  $V 49 = XX \textit{Cygni}$  <sup>4)</sup>, are all real, may be questioned; and likewise whether this is the case with the numerous secondary inflexions, which many authors draw in the light-curves of the Cepheids observed by them.

I propose to discuss the question whether as a *rule* the light-curves of the Cepheids can be drawn smooth and tense, and whether the period and the extent of the light-variation may as a *rule* be considered so nearly constant that a mean light-curve may be constructed. The question is of importance also for this reason that in the pulsation theory, which is founded on a physical base, secondary undulations are more

readily accepted than in the purely geometrical double star theory. It may, however, be pointed out that also in the latter there is every reason to assume physical disturbances of the smooth geometric process, since the spectrum is known to change<sup>5)</sup>.

It seemed of importance to discuss the errors occurring in my Cepheid curves, and to compare them with the errors of the Algol variable curves, which for obvious reasons must be drawn smooth and tense.

Too often the term secondary wave is erroneously applied to what is simply an effect of errors of observation; the astronomical literature presents numerous examples of this misunderstanding. In my opinion, this is due to two different causes.

First of all a light-curve is often founded on too few observations. LAU<sup>6)</sup> derives a light-curve of  $\eta$  Aquilae from only 56 estimates; the existence of a deep secondary wave appears to be dependent on the reliability of *two* successive observations, both giving a smaller brightness than corresponds with a smooth curve. KIESS<sup>7)</sup> derives a curve of  $V12 = RT$  Aurigae from 66 photometric observations, and assumes in it no less than 3 secondary undulations of a depth of  $0^m.1$ , which cannot but make a somewhat arbitrary impression; the curve would present a totally different aspect when a different grouping to normal places had been chosen. About this point and in general about the way in which the observations have been reduced, KIESS leaves us in the dark. At all events it seems impossible, that these not over-accurate observations (the mean error is  $0^m.13$ ) could say anything with certainty about undulations of  $0^m.1$ .

In the second place the curve traced follows the observations *too closely*; the amount of the inevitable errors of observation is accordingly not sufficiently taken into account. A striking example is furnished by SPERRA<sup>8)</sup>, whose curve of  $V23 = SW$  Draconis follows the normal places, as if there were no errors of observation at all. In the same number of the *Astronomische Nachrichten* ICHINOHE publishes a curve of  $V26 = SZ$  Aquilae, in the descending branch of which he assumes a hump; if, however, the curve is drawn smooth, the deviations are no greater, nay, even smaller than ICHINOHE himself allows in the neighbourhood of the minimum. LEINER speaks of a "scharf ausgeprägte sekundäre Welle" in the light-curve of  $V42 = VX$  Cygni, while a glance at the plotted normal places leads to the conviction that there is at least as much room for some other inflexions not assumed by LEINER, and that a smooth curve leaves deviations, which are perfectly admissible.

It is self-evident that the mean error must decide the question in every particular case, but, strange enough, this is often not given by the authors, so that any possibility of control is wanting.

In order to arrive at an impartial judgment, four conditions should in my opinion be observed as accurately as possible:

1. The algebraic sum of the deviations  $\delta$  (normal point minus curve) should be 0;

2. an equal number of plus and minus signs should be found in the series of deviations, and likewise

3. an equal number of permanences of sign and of variations;

4. the mean error  $\epsilon_0$  derived *a posteriori* from the deviations  $\delta$  should not be much greater than the m. e.  $\epsilon_1$ , which is to be expected *a priori* on account of the internal agreement of the normal places, and which follows from the m. e.  $\epsilon$  of one observation through division by  $\sqrt{m}$  (where  $m$  is the number of observations of a normal place).

If on these conditions a tense curve can be drawn, it is improbable that real significance should be assigned to the secondary waves, and it is preferable to leave them alone for the present, and direct one's full attention to the main problem.

Probably — but unfortunately this cannot be verified —  $\epsilon_0$  is considerably *smaller* than  $\epsilon_1$  in the cases cited above, and this would be irreconcilable with the circumstance, that in the derivation of  $\epsilon_0$  always new systematic errors occur, so that necessarily  $\epsilon_0$  must be found greater than  $\epsilon_1$ .

In a total of 19 light-curves (17 Cepheids)<sup>10</sup> I met with only two cases (*S Sagittae* and  $\eta$  *Aquilae*), where secondary waves could not be dispensed

	Cepheids	Algol-stars
m. e. $\epsilon$ of an observation	0 <sup>m</sup> .104	0 <sup>m</sup> .125
m. e. $\epsilon_1$ of a normal place	0.029	0.036
m. e. $\epsilon_0$ (normal place minus curve)	0.031	0.046
number of plus signs	135	353
.. noughts	86	124
.. minus signs	129	363
.. permanences	111	373
.. variations	153	343

with. The table shows in how far the above-mentioned conditions are satisfied. For a comparison the results of a discussion of 36 Algol-stars \*) have been added (see further on).

Two remarks about the Cepheids should be made here. First of all  $\epsilon_0$  appears to be about equal to  $\epsilon_1$ , though in consequence of the appearance of new systematic errors it might be expected that  $\epsilon_0$  would come out considerably greater. It should further be noted that the number of permanences is much smaller than the number of variations. It follows from both remarks that, though only twice a secondary wave was

\*) Besides these 36 there are still ten ready for publication, but it will not be easy to find the necessary funds to publish this bulky material *in originali*

assumed, yet in general the curves followed the normal points still too closely, and should have been drawn still tenser. The smoothing down of the curves gives rise to permanences, since the inflexions, that are removed, are based on at least two normal places: indeed, if an inflexion should be founded on only one normal place, it will not be accepted as real, for fear of falling into the error committed by LAU.

This is in my opinion the cause of the secondary waves which many observers, erroneously as it seems to me, assume to be a real phenomenon in their light-curves, whereas they should simply be taken as permanences of sign, which must necessarily occur according to the laws of chance, even when the phenomenon under examination should have to be represented by a perfectly smooth curve: every curve based on observations must exhibit secondary waves, even though the phenomenon observed does not in any way give rise to them.

By way of check it seemed interesting to examine the available Algol-stars with respect to the errors of their light-curves, since these must certainly be drawn tense. These stars have been observed in exactly the same way, with the same instruments and by the same observer as the Cepheids. The results are placed side by side with those of the Cepheids. That the number of permanences is equal to that of the variations suggests a normal distribution of errors.

For the Algol-stars the great value of the mean errors should be noted.

a. First of all the m.e.  $\varepsilon$  of one observation (hence also the m.e.  $\varepsilon_1$  of a normal place, generally formed from 12 observations) is considerably greater with the Algol-stars than with the Cepheids. I am inclined to attribute this to a greater influence of the systematic errors. The normal place has been derived from observations of somewhat different phases, and this may greatly increase the m.e., especially where the curve has a very steep course. It is true, that just as with the Cepheids<sup>11)</sup> many normal places have been excluded from the discussion for this reason, but probably I did not go far enough in this procedure, so that a number of normal places were allowed to contribute to the result, whose m.e. are vitiated, i.e. increased by the systematic error indicated just now.

It may be further noted that in watching an Algol-star the observer is unfortunately often prejudiced to a certain extent; it is practically impossible to prepare for the minimum without an at least approximate knowledge of the epoch of the expected phenomenon, and it is exceedingly difficult to emancipate oneself entirely from this knowledge in making the observations.

b. In the second place it will be noticed that the ratio  $\frac{\varepsilon_0}{\varepsilon_1}$  is 1.28 for the Algol-stars, and only 1.07 for the Cepheids. In consequence of the inevitable systematic errors  $\varepsilon_0$  must be greater than  $\varepsilon_1$ , and I am inclined to ascribe these errors in the case of the Algol-stars chiefly

to the necessity of drawing the curves smooth. Probably the m.e.  $\epsilon_0$  is not too great for the Algol-stars, but on the contrary too small for the Cepheids: and thus we arrive again at the conclusion that the curves of the Cepheids seem to follow the normal places too closely, and should have been drawn tenser.

Finally it seemed desirable to test the distribution of the errors of observation by the exponential law of GAUSS. As error of observation the deviation "observation minus normal place" was taken, increased by the deviation "normal place minus curve". Both for the Cepheids and the Algol-stars the negative and the positive errors proved to follow exactly the same law, so that the frequency curves could be drawn symmetrically. Both curves present the typical deviation from the exponential curve, consisting in an excess of the very small and of the very great errors, whereas the number of the moderately great errors is too small.

## CEPHEIDS.

Number of errors: 4288 m. e. $\epsilon$ of an observation: 0 <sup>m</sup> .102					$h = \frac{1}{\epsilon\sqrt{2}} = 6.932$				
a	n	$n_w$	$n_E$	$n_w - n_E$	a	n	$n_w$	$n_E$	$n_w - n_E$
± 0.00	192	192	167	+ 25	± 0.22	39	31	33	- 2
01	386	382	333	+ 49	23	22	25	26	- 1
02	388	374	328	+ 46	24	19	22	22	0
03	353	360	321	+ 39	25	12	19	18	+ 1
04	318	340	310	+ 30	26	21	16	14	+ 2
05	323	315	297	+ 18	27	13	14	12	+ 2
06	296	291	282	+ 9	28	6	12	9	+ 3
07	275	266	265	+ 1	29	12	11	7	+ 4
08	241	236	246	- 10	30	14	9	5	+ 4
09	181	206	227	- 21	31	9	8	3	+ 5
10	167	177	207	- 30	32	4	7	2	+ 5
11	150	152	187	- 35	33	2	6	1	+ 5
12	152	135	168	- 33	34	3	5	1	+ 4
13	117	120	149	- 29	35	6	5	1	+ 4
14	109	105	131	- 26	36	5	4	1	+ 3
15	105	93	114	- 21	37	0	3	0	+ 3
16	82	80	98	- 18	38	4	3	0	+ 3
17	70	69	84	- 15	39	0	2	0	+ 2
18	47	60	71	- 11	40	0	2	0	+ 2
19	50	50	59	- 9	41	0	1	0	+ 1
20	48	43	49	- 6	42	1	1	0	+ 1
21	46	36	40	- 4		4288	4288	4288	

$$x_1 = 0^m.070 = 0.65 \epsilon$$

$$x_2 = 0 .240 = 2.36 \epsilon$$

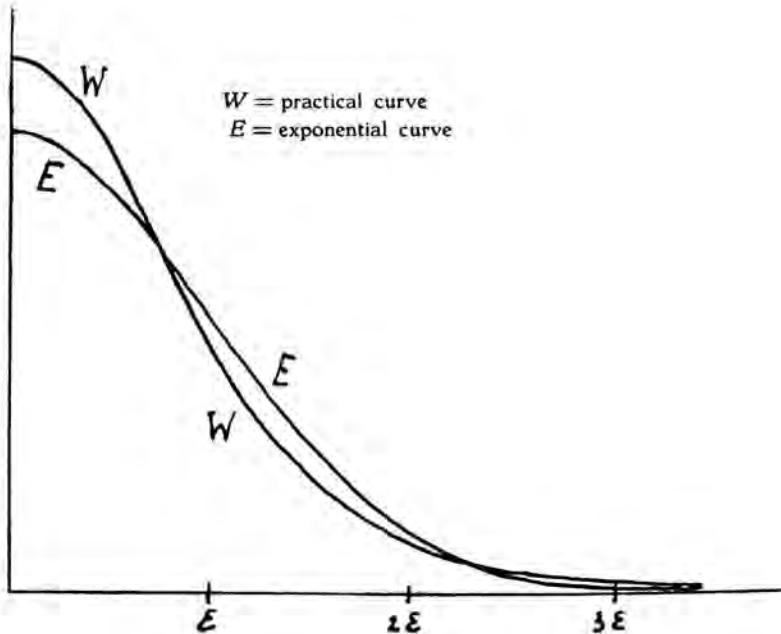
## ALGOL-STARS.

Number of errors: 9955 m. e. $\epsilon$ of an observation: 0 <sup>m</sup> .132					$h = \frac{1}{\epsilon\sqrt{2}} = 5.348$				
$a$	$n$	$n_w$	$n_E$	$n_w - n_E$	$a$	$n$	$n_w$	$n_E$	$n_w - n_E$
± 0.00	335	340	300	+ 40	± 0.34	29	32	22	+ 10
01	712	676	600	+ 76	35	26	28	18	+ 10
02	632	670	593	+ 77	36	26	24	15	+ 9
03	588	650	585	+ 65	37	28	21	12	+ 9
04	589	622	574	+ 48	38	16	18	9	+ 9
05	601	595	559	+ 36	39	11	16	8	+ 8
06	543	566	542	+ 24	40	12	14	6	+ 8
07	597	530	523	+ 7	41	6	12	5	+ 7
08	517	492	499	- 7	42	14	11	4	+ 7
09	458	457	477	- 20	43	6	9	3	+ 6
10	426	421	451	- 30	44	15	8	2	+ 6
11	400	385	425	- 40	45	6	6	2	+ 4
12	335	349	397	- 48	46	3	4	2	+ 2
13	336	315	371	- 56	47	6	4	1	+ 3
14	263	287	344	- 57	48	7	4	1	+ 3
15	292	263	314	- 51	49	2	3	1	+ 2
16	252	239	289	- 50	50	8	3	1	+ 2
17	228	219	265	- 46	51	2	3	0	+ 3
18	175	201	237	- 36	52	1	3	0	+ 3
19	179	183	214	- 31	53	2	2	0	+ 2
20	179	165	191	- 26	54	4	2	0	+ 2
21	150	150	171	- 21	55	1	2	0	+ 2
22	147	136	150	- 14	56	2	2	0	+ 2
23	116	123	132	- 9	57	1	2	0	+ 2
24	113	110	116	- 6	58	0	1	0	+ 1
25	84	98	101	- 3	59	1	1	0	+ 1
26	89	87	87	0	60	0	1	0	+ 1
27	80	78	74	+ 4	61	4	1	0	+ 1
28	57	69	64	+ 5	62	1	1	0	+ 1
29	73	61	54	+ 7	63	0	1	0	+ 1
30	49	53	46	+ 7	64	0	0	0	0
31	36	47	39	+ 8	65	1	0	0	0
32	39	41	32	+ 9		9955	9955	9955	
33	44	36	27	+ 9					

$$x_1 = 0^m.076 = 0.58 \epsilon$$

$$x_2 = 0^m.260 = 1.97 \epsilon$$

In the tables (see p. 146 and p. 147) the actually observed numbers  $n$  are given, graphically smoothed down to  $n_w$ ; they have been compared with the values  $n_\varepsilon$  following from the exponential law. The errors 0.00,



0.01, 1.02 etc. are supposed to lie between the limits 0.00 and  $0.00^5$ ,  $0.00^5$  and  $0.01^5$ ,  $0.01^5$  and  $0.02^5$  etc.

The tables show first that, in accordance with the greater m.e., the greater extreme cases occur with the Algol-stars. It may seem strange that it is possible to make errors of  $0^m.5$  and  $0^m.6$ , but according to the law of the great numbers such extreme cases, more than four times the m.e., must now and then occur in a series of almost 10.000 observations. In the second place we may remark, that for the Cepheid series the abscissae\*) of the points of intersection of the exponential with the actually observed curve almost entirely satisfy the remarkable equation <sup>12)</sup>:

$$\left(\frac{x}{\varepsilon}\right)^2 - 6\left(\frac{x}{\varepsilon}\right) + 3 = 0.$$

From this it follows:

$$\left. \begin{aligned} x_1 &= 0.74 \varepsilon = 0^m.076 \\ x_2 &= 2.33 \varepsilon = 0^m.238 \end{aligned} \right\} \text{for } \varepsilon = 0^m.102,$$

the observed points of intersection lying at  $0^m.070$  and  $0^m.240$ . For the Algol-stars  $\varepsilon = 0^m.132$ , hence the points of intersection would be expected at

\*) Here the positive values are only considered.

$0^m.098$  and  $0^m.308$ , whereas they are really found at  $0^m.076$  and  $0^m.260$ . That both points lie so much nearer the  $Y$ -axis than follows from the above equation may be ascribed — as is evident from the figure — to a too small number of small errors (smaller than that actually observed, though still much greater than the theoretical number) and a too great number of great errors. This may readily be ascribed to the influence of the systematic errors "normal place minus curve", which give rise to considerable corrections in the Algol-curves, since they must necessarily be drawn smooth.

### CONCLUSION.

Apart from two exceptional cases there is no urgent reason, why the curves of the examined Cepheids should not be drawn perfectly smooth and tense. The remaining errors appear to behave — in a still greater degree than those of the Algol-curves — entirely as accidental errors. If, as many observers assert, there is hardly question of a mean curve at all for the Cepheids on account of the numerous irregularities of all kinds, these irregularities are entirely hidden in the errors of observation; they do not spoil their accidental character, nor do they appreciably increase their amount.

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**Physics.** — “*The Evershed effect in the spectrum of sun-spots*”. By Prof. W. H. JULIUS<sup>1)</sup>.

(Communicated at the meeting of January 31, 1925).

A well-defined general property of Fraunhofer lines is their systematic deformation in the spot-spectrum, known as the „Evershed effect”.

About 1909 EVERSLED observed<sup>2)</sup> that, if the slit of the spectrograph bisects a sun-spot in a direction passing through the centre of the solar disc, the lines of the spot-spectrum are systematically displaced, towards the red at the peripheral edge, towards the violet at the central edge of the spot. These displacements are small if the spot is located not far from the centre of the disc and increase as the limb is approached; their magnitude depends in a special manner upon the intensity of the lines and increases in general with the wave-length, but not proportionally. If the slit cuts the spot in other directions, similar displacements are observed, though smaller and less systematic; least when the slit is perpendicular to the radius of the disc. The hydrogen line  $H\beta$  did not show the displacement, and a few other strong chromospheric lines seemed to be displaced in a direction opposite to the regular shift<sup>3)</sup>.

It is known that EVERSLED has interpreted these phenomena as indicating motion of the absorbing gases from the umbra radially outwards, tangential to the solar surface, with velocities that increase until the outer limit of the penumbra is reached, where the motion is rather abruptly stopped.

This interpretation seemed to account fairly well for the principal characteristics of the phenomenon. It is accepted and elaborated in detail by ST. JOHN<sup>4)</sup> using a rich observational material collected on Mount Wilson in addition to the original Kodaikanal data. If one holds the view — taken by both observers — that the solar spectrum is a pure absorption phenomenon, it seems in fact impossible to explain the Evershed effect without having recourse to the Doppler principle; other causes of line

<sup>1)</sup> Soon after deliverance of the proof of this paper to Prof. JULIUS for correction for press, the Academy, to its great sorrow, received the announcement of his death on April 15, 1925.

<sup>2)</sup> EVERSLED, Kodaikanal Bulletin XV, 1909.

<sup>3)</sup> In still another respect the lines  $H_{\alpha}$  of hydrogen and  $H$  and  $K$  of calcium behave differently from the rest: their displacement begins over the photosphere, outside the penumbral region, and is not always very clearly defined, owing to the width and irregularities at the edges of the line (Transactions of the International Union for co-operation in solar Research, Vol. IV, p. 129—130). Circumstances regarding those lines evidently require separate consideration.

<sup>4)</sup> ST. JOHN, Contrib. Mt. Wilson Obs. N<sup>o</sup>. 69 and 74; Astroph. Journ. **37**, 322, **38**, 341, 1913.

displacement, like pressure, electric or magnetic fields, cannot in any satisfactory way be made responsible for the peculiarities of the phenomenon.

But now it had to be ascertained how far the necessary consequences of that Doppler explanation would prove compatible with the results of further observations, for instance with the fact that over spot umbrae the displacements are very small and uncertain in direction, nay indicating descent in the majority of cases. That serious difficulties are here encountered, I believe to have sufficiently shown on a former occasion<sup>1)</sup>, to justify the attempt to give due attention to an entirely different interpretation of the phenomenon.

It is indeed not necessary to suppose that the darkness of Fraunhofer lines is caused by absorption alone. We may keep in view the possibility that in the solar spectrum we are dealing with *dispersion lines*<sup>2)</sup>, in which the distribution of the light is governed by the sinuosity of rays in a medium, the optical density of which varies very irregularly in general — but rather systematically in the regions of sun-spots.

On the basis of this hypothesis too an interpretation of the Evershed effect, accounting for its most characteristic features, could be given. As a substitute for the dynamical conception of the spot, with its permanent hurricanes of many kilometers per second wind velocity — required by the absorption theory — the dispersion hypothesis introduces a rather statical conception, in which differences of density and composition determine the optical phenomena, and motion may be much slower<sup>3)</sup>.

After the ample observations communicated by ST. JOHN in the years 1913—1915 not many new data on the Evershed effect have appeared; only one important article, published by EVERSHERD himself in *Kodaikanal*

<sup>1)</sup> JULIUS, *Astroph. Journ.* **40**, 1, 1914; **43**, 43, 1916.

<sup>2)</sup> In support of this theory of the solar spectrum we call to mind the following results of recent inquiry: 1. The new ideas on atomic structure are also leading to the view that the spectral regions where true absorption can take place are much narrower than was formerly believed (BOHR, *Zeitschr. f. Phys.* **13**, 162, 1923). 2. At all levels in the sun where Fraunhofer lines are supposed to originate, the pressure must be very low, much less than 1 atm. (ST. JOHN and BABCOCK, *Astroph. Journ.* **60**, 32, 1924). 3. For the limb-centre displacements no other explanation besides the one following from the dispersion theory seems to hold (JULIUS, *Zeitschr. f. Phys.* **27**, 23, 1924). 4. In an article on "Ionisation in stellar atmospheres" A. PANNEKOEK also concludes that in addition to selective absorption and molecular scattering there must be active in the sun another cause of extinction, at least ten times as effective as molecular scattering (B. A. N. **19**, 1922, p. 113). 5. From the defect of perspective foreshortening in spectro-heliograms (These Proceedings **27**, 451, 1924), and from stereoscopic observation of such documents we may infer that the photosphere must be transparent down to considerable depth.

<sup>3)</sup> From this point of view the Evershed effect has for the first time been dealt with in these Proceedings **12**, p. 278—279, 1910; more amply in *Astroph. Journ.* **40**, 1—32, 1914, and **43**, 43—66, 1916. The idea was then opposed by ST. JOHN, in *Contrib. Mt. Wilson Nos* 93 and 123 or *Astroph. Journ.* **41**, 28, 1915 and **44**, 1916, and again defended by the author in several articles on the dispersion theory of Fraunhofer lines (*Verslag Akad. v. Wet. Amsterdam*, **25**, 1245, 1917; These Proceedings **23**, p. 1113, 1921; **26**, p. 329, 1923; *Astroph. Journ.* **54**, 92, 1921).

*Bull.* 51, 1916, has yet revealed certain peculiarities of the phenomenon which one has to keep in mind in any attempt to explanation. EVERSHED, in fact, adheres to the interpretation of the displacements as Doppler effects, but not without calling attention to some difficulties to which this leads.

The new data we have to consider bear upon a large spot which crossed the disc in  $21^\circ$  northern latitude between March 29<sup>th</sup> and April 12<sup>th</sup> 1915. The seeing was excellent. EVERSHED emphasizes that the displacements are larger with good definition of the penumbral image than would have been the case with an image more or less diffused along the slit by poor definition or long exposure time. So the characteristics of the phenomenon could be more sharply noticed than on former occasions. The computed horizontal radial velocities were found about 2.7 times larger than those observed by ST. JOHN for the corresponding line intensities — a discrepancy which is probably mainly accounted for by difference in magnitude of the observed spots or by unequal diffusion of the spot image on the slit-plate.

It was an important feature of these observations that the displacements have been measured *separately* at the opposite outer limits of the penumbra, each with respect to the average position of the line outside the spot (whereas ST. JOHN only gave the sums of the opposite displacements). Selected for measurement were a great many *Fe*-lines of intensities ranging from 0 to 6 of ROWLAND'S scale, and besides a few lines of *Ni*, *Cr*, and *Ti*. The spot passed the meridian on April 4–5; several spectra were obtained before and after that passage and measurements made on 11 plates in total.

The known relation between the magnitude of the displacements and the line intensity showed quite clearly again; the shifts were greatest for intensities 0 and 1; they decreased as the intensities rose to 5 and 6. Moreover, a remarkable fact presented itself, which had not been noticed before: viz. that *the displacements were systematically greater in the penumbra directed towards the limb*. As on that side the shift is always towards the red, we may also state: *the displacements towards the red were systematically greater than those towards the violet*.

EVERSHED gives no explanation of this remarkable fact; he suggests that it may be an accidental circumstance, although the same phenomenon appears on some of his previous measures. The following table shows clearly, though, that the inequality is considerable and holds for all line intensities. Mean results are here given of a great number of observations relating to different positions of the spot on the disc and to various spectral regions. The figures represent kilometers per second, reduced to horizontal movement at the outer edges of the penumbra; the positive sign corresponds to receding motion.

On the basis of the Doppler interpretation we are thus led to the enigmatic conclusion that in the spot there would always be an excess of motion directed towards the limb of the solar disc. It appears im-

possible to conceive a circulatory process answering that peculiar condition, whatever vertical velocity components one might imagine for complementing the radial motion. This impossibility condemns the radial motion hypothesis.

April 3, Spot East			April 6 and 7, Spot West.	
Line intensity	East penumbra	West penumbra	East penumbra	West penumbra
0 en 1	+ 2.73	- 2.02	- 1.41	+ 3.23
2	+ 2.19	- 2.04	- 1.21	+ 2.84
3	+ 2.14	- 1.59	- 1.08	+ 2.49
4	+ 2.02	- 1.66	- 1.06	+ 2.39
5 en 6	+ 1.09	- 1.41	- 0.90	+ 1.98

We are going to show that the dispersion theory of Fraunhofer lines suggests an adequate explanation of the observed peculiarity.

First, however, we should mention a few remarks made by EVERSHED with regard to line displacements observed when the slit was perpendicular to the radius of the solar disc.

On April 1 (spot near east limb) a shift was observed towards the red in the southern penumbra only; interpreted as a horizontal movement it would indicate a velocity of 0.64 km/sec. Two hours later: nearly equal displacements in north and south penumbrae, both about 0.46 km/sec.

On April 2 the same spot showed displacement towards the red at its northern edge only, corresponding to 0.9 km/sec. horizontal velocity; in the southern penumbra there was a slight shift towards the violet, 0.1 km/sec.

These displacements cannot represent a rotational movement of the spot, as the northern and southern shifts are not opposite. After the spot had passed the meridian, on April 9, a similar exposure with tangential slit gave, however, fairly opposite displacements north and south; reduced to horizontal movement:

northern penumbra: 0.65 km/sec.,

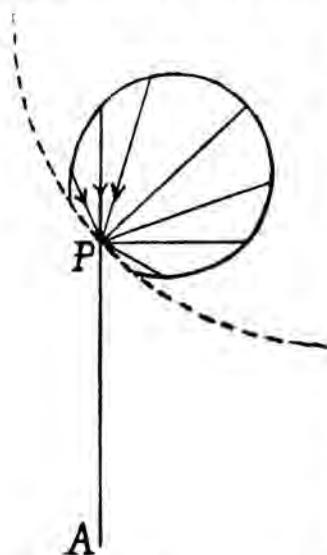
southern penumbra: - 0.88 km/sec.

Let us now suppose that this does represent a rotation, with a mean velocity of 0.77 km/sec. at the outer edge of the penumbra. The diameter of the spot was 41000 km.; a complete rotation would have taken 46 hours; so one might have expected a visible rotation of the (irregular) spot in a reasonable time. There was, however, no evidence of such change, when comparing the shape of the spot on successive days. Moreover, the direction of the rotation would not correspond to that found by HALE from the magnetic polarity of the spot. EVERSHED, therefore, considers it

to be doubtful whether these line displacements really indicate rotation of the gases over the spot; he can only ascribe them to fortuitous, irregular movements.

It deserves notice that neither about the origin, nor about the consequences of violent solar storms (rotational or radial) any other evidence besides line displacement has ever been given by the observations. The circulatory system imagined by EVERSLED and ST. JOHN cannot, therefore, be said to constitute a necessary link in some series of conceptions; it depends entirely on the arbitrary hypothesis that the shifts are a Doppler effect. So we may safely abolish that supposition if we can dispense with it, as no connexion with other phenomena is thus broken.

Let us now consider the matter from the point of view of the dispersion theory. We start from the conception that in a sun-spot the optical density varies altogether irregularly, but increases on the average from the umbra outwards. Such a distribution of matter, existing in front of a luminous sphere, must show a peculiar distribution of light much like the known aspect of the umbra and penumbra of a sunspot. This could easily be explained geometrically using simple diagrams, and demonstrated by means of experiments with liquid drops of different refractive power<sup>1)</sup> and with whirling masses of gas<sup>2)</sup>. From this conception of the nature of a sun-spot follows immediately, without any additional hypothesis, an explanation of the shifts of the Fraunhofer lines in the spot spectrum;



we only have to take into account the unequal refractivity of the *R*-light and the *V*-light in the surroundings of each absorption line, and the characteristics of the Evershed effect will at once become manifest<sup>3)</sup>.

The following representation of the rather intricate refracting process appeals perhaps somewhat more to the mind than the one given on former occasions, though it essentially rests on exactly the same principle.

Let *P* be a point somewhere in the solar atmosphere. It receives light from the various directions in quantities proportional to the radii vectores of the „surface of irradiation“<sup>4)</sup> (the mean shape of which is known from direct measurement of the distribution of brightness over the solar disc). We have to consider the properties of the light which, after having suffered ir-

<sup>1)</sup> These Proceedings 12, 206, 1909.

<sup>2)</sup> Physik. Zeitschr. 15, 48, 1914.

<sup>3)</sup> Astroph. Journ. 40, (especially p. 19—25) 1914, and 43, 43—66, 1916.

<sup>4)</sup> Handwörterbuch d. Naturwissenschaften VII. 830, 1912.

regular refraction in the region about  $P$ , emerges in the direction  $PA$  towards the earth. As regards the position of  $P$  in the spot region we distinguish the following two cases:

a.  $P$  is situated in the penumbra nearest to the sun's limb. According to our supposition the density is everywhere irregular, so that there are gradients in all directions. A gradient will be designated  $+$  or  $-$  if the density is either increasing or diminishing towards the edge of the disc.

Consider the action of an arbitrary  $+$  gradient on a certain  $R$ -light and a certain  $V$ -light, selected so as to have equal values of  $n-1$ . Then the  $R$ -light must have come from the left, the  $V$ -light from the right side; and, owing to the peculiar shape of the surface of irradiation, we immediately see that the weakening suffered by the  $R$ -light must be somewhat greater than the strengthening of the  $V$ -light.

Next consider the action of an arbitrary  $-$  gradient on the same selected kinds of light. Now, with equal angular deviations, the weakening of the  $V$ -light will be more considerable than the strengthening of the  $R$ -light.

In both cases, therefore, if  $R$ -light and  $V$ -light are taken together, the joint result is a weakening. But because  $P$  is in the peripheral half of the penumbra, where the  $+$  gradients are on the average higher than the  $-$  gradients, the weakening of the  $R$ -light will be greater than the weakening of the  $V$ -light. This manifests itself as a displacement of the line towards the red.

b.  $P$  be situated in the penumbra farthest from the sun's edge. We again distinguish the case of a  $+$  gradient and a  $-$  gradient, and find once more that the weakening always predominates. At present, however, we are dealing with a region where the  $-$  gradients have the advantage over the  $+$  gradients, and where, therefore, the  $V$ -light will be more weakened than the  $R$ -light; the line appears to be shifted towards the violet.

The principal feature of the Evershed effect is thus accounted for. But what about the peculiarity afterwards stated, that on the peripheral edge of the spot the displacements are always greater than on the central edge?

This result too is easily understood on the basis of the dispersion theory. We are concerned with a consequence of the same circumstance upon which also depend the general displacement of Fraunhofer lines towards the red, and the limb—centre displacements in particular.

Indeed, the intensity of refraction effects is determined, for each wave-length, by the corresponding value of  $n-1$ . This quantity varies strongly in passing every absorption line; but as on an average the refractive index of the solar gases is greater than 1, the absolute value of  $n-1$  will, as a rule, be greater on the red than on the violet sides of the absorption lines. And stronger irregular refraction generally involves

increased weakening; so the average value of the shifts towards the red must exceed that of the shifts towards the violet.

It is interesting to notice that this single principle — which causes Fraunhofer lines to be asymmetrical to a degree fluctuating through the spectrum — correlates several classes of systematic line displacements, namely the general sun-arc displacements, the limb-centre shifts, and the preponderance of displacements towards the red in the Evershed effect. A very marked excess of displacements towards the red has also been found in prominences both at the limb and in disturbed regions on the disc <sup>1)</sup>; it is not improbable that this is due to the same cause.

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<sup>1)</sup> Transactions of the International Union for co-operation in Solar Research, Vol. IV, p. 128, 1914.

**Chemistry.** — “Equilibria in systems, in which phases, separated by a semi-permeable membrane.” IV. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of December 27, 1924.)

*Ternary equilibria with solid phases.*

In the previous communication we have discussed the *O.W.A.* (osmotic water-attraction) etc. of liquids in ternary systems, when one of the components occurs as solid phase. Now we shall assume that a binary compound viz. a hydrate component *Y* occurs.

The saturation-curve of this hydrate is represented for a definite *T* and *P* by curve *w d v*; point *H* represents the hydrate; every straight line starting from point *H* is allowed to intersect this curve in one point only. We shall call *w* the terminating-point of the curve rich in water and *v* the terminating-point poor in water. Just as in the previous communication we shall say also here that point *a* is situated closer to *w* than *b*, etc. It is not allowed, however, to prove from this (compare the previous communication) that a liquid of this curve contains the more (less) water, the closer (further) it is situated to (from) the point *w*. The dotted curves *w m*, etc. are the isotonic *W*-curves.

In a similar way as in the previous communication we may deduce:

1<sup>o</sup>. An isotonic curve and the saturation-curve of the hydrate can intersect one another in one point only, they never can touch one another.

2<sup>o</sup>. The *O.W.A.* of a liquid of a saturation-curve of a hydrate is greater (smaller) the more this liquid is situated further from (closer to) the terminating-point rich in water of this curve.

The *O.W.A.* increases, therefore, along curve *w v* in the direction of the arrows.

3<sup>o</sup>. An isotonic curve and the saturation-curve of a hydrate are situated in the vicinity of their point of intersection either both within the conjugation-angle or both within the supplement-angle. When the one curve touches one side of that angle, than the other curve touches the other side.

In point *c* (fig. 1) the conjugation-angle is *W c H*; as the saturation-curve touches *WC* in *c*, the isotonic curve *n n'* must touch *cH* in *c*.

We are able to deduce the property mentioned sub. 2<sup>o</sup> a.o. also in the following way. When we represent the composition of *H* by:  $\beta \text{ Mol } Y + (1 - \beta) \text{ Mol } W$ , then the saturation-curve *w v* is defined by:

$$\zeta - x \frac{\delta \zeta}{\delta x} + (\beta - y) \frac{\delta \zeta}{\delta y} = \zeta_H \dots \dots \dots (1)$$

in which  $\zeta_H$  is the  $\zeta$  of the substance  $H$ . The *O.W.A.* of a liquid is defined by:

$$\varphi = \zeta - x \frac{\delta \zeta}{\delta x} - y \frac{\delta \zeta}{\delta y} \dots \dots \dots (2)$$

From (1) follows:

$$[-x r + (\beta - y) s] dx + [-x s + (\beta - y) t] dy = 0 \dots \dots (3)$$

From (2) follows in connection with (3)

$$\frac{1}{\beta} d\varphi = -s dx - t dy \dots \dots \dots (4)$$

We now take a system of coordinates with the point  $H$  as pole and the line  $HW$  as axis; we represent the radius vector by  $\varrho$  and the angle by  $\mu$ ; consequently in  $w$  is  $\mu = 0$ , in  $v$  is  $\mu = 180^\circ$ . In order to simplify the calculation we imagine angle  $WXY = 90^\circ$ , which has not any influence on the result. We now have:

$$\begin{aligned} \varrho \sin \mu &= x & \varrho \cos \mu \cdot d\mu + \sin \mu \cdot \delta \varrho &= dx \\ \varrho \cos \mu &= \beta - y & -\varrho \sin \mu \cdot d\mu + \cos \mu \cdot \delta \varrho &= -\delta y. \end{aligned}$$

When we substitute those values in (3) and (4) then follows:

$$\begin{aligned} \varrho [(t - r) \sin \mu \cdot \cos \mu + s (\cos^2 \mu - \sin^2 \mu)] d\mu &= \delta \varphi \\ &= [r \sin^2 \mu - 2s \sin \mu \cos \mu + t \cos^2 \mu] d\varrho \end{aligned} \dots \dots (5)$$

$$\frac{1}{\beta} \cdot \delta \varphi = -\varrho (s \cos \mu + t \sin \mu) d\mu - (s \sin \mu - t \cos \mu) \delta \varrho \dots (6)$$

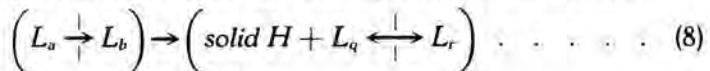
Outside a region of dimixtion  $rt - s^2$  and consequently also the coefficient of  $\delta \varrho$  in (5) is always positive and never zero; therefore  $\delta \mu$  can not become zero. A radius vector going through point  $H$ , therefore never can touch the saturation-curve  $wv$ , only in one point it may intersect this curve.

By elimination of  $\delta \varrho$  it follows from (5) and (6):

$$\frac{d\varphi}{d\mu} = \frac{\beta \varrho (rt - s^2) \sin \mu}{r \sin^2 \mu - 2s \sin \mu \cos \mu + \cos^2 \mu} \dots \dots (7)$$

so that the second part of (7) is negative. Consequently  $\varphi$  decreases along curve  $wv$  starting from  $w$  towards  $v$ , so that *O.W.A.* increases starting from  $w$  towards  $v$ .

Point  $c$ , viz. the point of contact of the tangent to curve  $wv$  drawn from point  $W$ , divides  $wv$  into two parts. We now bring into osmotic contact two liquids  $L_a$  and  $L_b$  of part  $wc$ ; as  $L_b$  has a greater *O.W.A.* than  $L_a$ , water is diffusing from  $L_a$  towards  $L_b$ . Consequently the inversion is:



In this  $L_q$  represents a saturated solution between  $a$  and  $b$  and  $L_r$  an unsaturated solution; of course  $L_q$  and  $L_r$  are situated on the same osmotic curve.

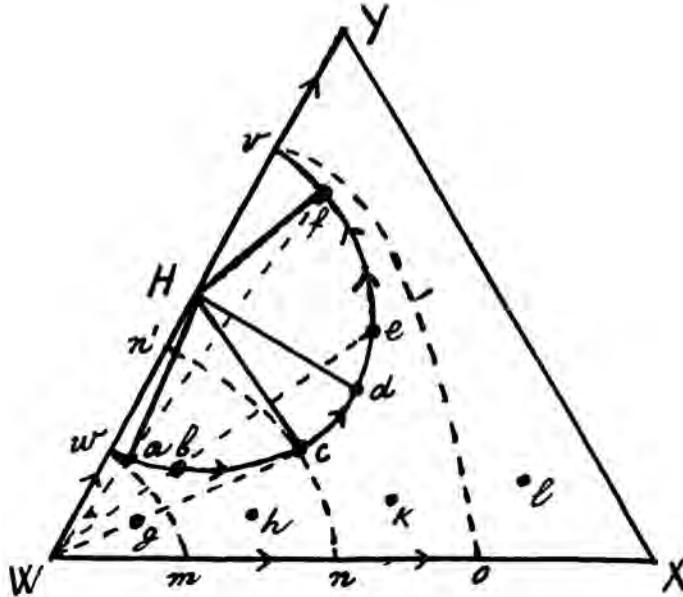
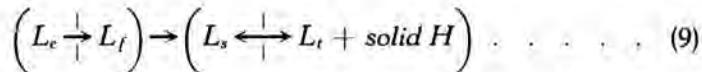


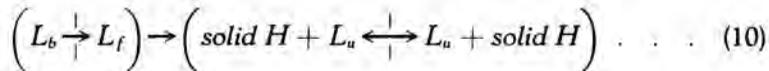
Fig. 1.

When we bring into osmotic contact  $L_e$  and  $L_f$  of part  $cv$ , then the inversion is:



in which  $L_t$  represents a liquid between  $e$  and  $f$  and  $L_s$  an unsaturated liquid.

When we take two liquids, the one of which is situated on part  $wc$  and the other on part  $cv$ , f.i.  $L_b$  and  $L_f$ , then the inversion is:



The position of  $L_u$  depends on the situation of the complex of  $L_b$  and  $L_f$ ; when f.i. this complex is situated on the line  $Hd$ , then is  $L_u = L_d$ .

With inversion (8) the solid substance arises on that side of the membrane on which water is removed from; in (9) on that side to which water is diffusing; in (10) the solid substance arises on both sides of the membrane.

We bring the two binary liquids  $L_w$  and  $L_v$  into osmotic contact. As  $L_v$  has a greater *O.W.A.* than  $L_w$  the inversion is:

$$\left( L_w \begin{array}{c} \downarrow \\ \uparrow \\ \downarrow \end{array} L_v \right) \rightarrow \left( \text{solid } H + L_w \begin{array}{c} | \\ | \\ | \end{array} \text{solid } H \right) \dots \dots \dots (11)$$

or :

$$\left( L_w \begin{array}{c} \downarrow \\ \uparrow \\ \downarrow \end{array} L_v \right) \rightarrow \left( \text{solid } H \begin{array}{c} | \\ | \\ | \end{array} L_v + \text{solid } H \right) \dots \dots \dots (12)$$

In both cases viz. water is diffusing from  $L_w$  towards  $L_v$  and  $L_w$  passes with loss of water,  $L_v$  with increase of water into solid  $H$ . This diffusion continues till all the liquid either on the one or on the other side of the membrane, has disappeared. When we bring  $L_w$  and  $L_v$  in definite ratio into osmotic contact, then the inversion may become also :

$$\left( L_w \begin{array}{c} \downarrow \\ \uparrow \\ \downarrow \end{array} L_v \right) \rightarrow \left( \text{solid } H \begin{array}{c} | \\ | \\ | \end{array} \text{solid } H \right) \dots \dots \dots (13)$$

The liquids then disappear on both sides of the membrane with separation of solid  $H$ .

We now bring into osmotic contact  $L_w$  with a liquid  $L_q$ ; consequently we have a system  $\left( L_w \begin{array}{c} | \\ | \\ | \end{array} L_q \right)$ . In the same way as in the previous communication it now appears :

1<sup>o</sup>. when  $L_q$  is situated within the region  $Wwm$ , then water is diffusing from  $L_q$  to  $L_w$ ; then  $L_w$  passes into an unsaturated liquid between  $w$  and  $W$ .

2<sup>o</sup>. when  $L_q$  is situated on the isotonic curve  $wm$ , then  $L_q$  and  $L_w$  are in osmotic equilibrium and nothing happens.

3<sup>o</sup>. when  $L_q$  is situated within the region  $wmXYvdw$ , then water is diffusing from  $L_w$  to  $L_q$ ; then  $L_w$  shall separate the substance  $H$  and shall dry up totally or partially.

When we bring  $L_v$  into osmotic contact with a liquid  $L_q$ , then we have to bear in mind that, as appears also from fig. 1,  $L_v$  separates the solid hydrate  $H$  with increase of water, and that  $L_v$  passes into an unsaturated solution losing water.

We now find :

1<sup>o</sup>. when  $L_q$  is situated within the region  $WovdwW$ , then water is diffusing from  $L_q$  to  $L_v$ ; then  $L_v$  separates solid  $H$  and dries up totally or partially.

2<sup>o</sup>. when  $L_q$  is situated on the isotonic curve  $vo$  then nothing happens.

3<sup>o</sup>. when  $L_q$  is situated within the region  $voXY$  then water is diffusing from  $L_v$  to  $L_q$ ; then  $L_v$  becomes an unsaturated solution between  $v$  and  $Y$ .

Different results may be deduced from those considerations. A.o. this: all liquids within the region  $wmovidw$  make as well  $L_w$  as  $L_v$  to dry up totally or partially into the solid substance  $H$ .

In accordance with our definition of the osmotic water-attraction of solid substances (see the previous communication) we have to mean by the *O.W.A.* of the hydrate *H* the *O.W.A.* of the liquid which arises when a very small quantity of water is added to the substance *H*; consequently here this is the liquid  $L_w$ . Therefore curve *wm* is the curve (*O.W.A.* = *H*).

Just as in the previous communication we now find:

1°. the hydrate *H*, in osmotic contact with a liquid within the region *Wwm*, shall remove water from this liquid.

2°. the hydrate *H*, in osmotic contact with a liquid outside the region *Wwm*, can not remove water from this liquid.

Consequently when we bring solid *H* in osmotic contact with liquid  $L_g$  (fig. 1) then water diffuses to the solid substance and is formed either: solid  $H + L_w$  or an unsaturated liquid between *w* and *W*.

When we bring solid *H* in osmotic contact with one of the liquids *h*, *k*, *l*, *n* or *o* (fig. 1) then nothing happens. When, however, we bring in osmotic contact one of those liquids with  $L_w$ , then  $L_w$  is drying up totally or partially with separation of solid *H*.

In fig. 2 point *D* represents a ternary compound, f.i. a hydrus double-salt. The saturation-curve of *D* is represented by the closed curve *wbvfw*. In accordance with a well-known property all lines starting from point *D* intersect this curve in one point only. As *w* and *v* represent the solutions of *D* in pure water, we may call *w* the point of solubility of substance *D* rich in water and *v* the point poor in water

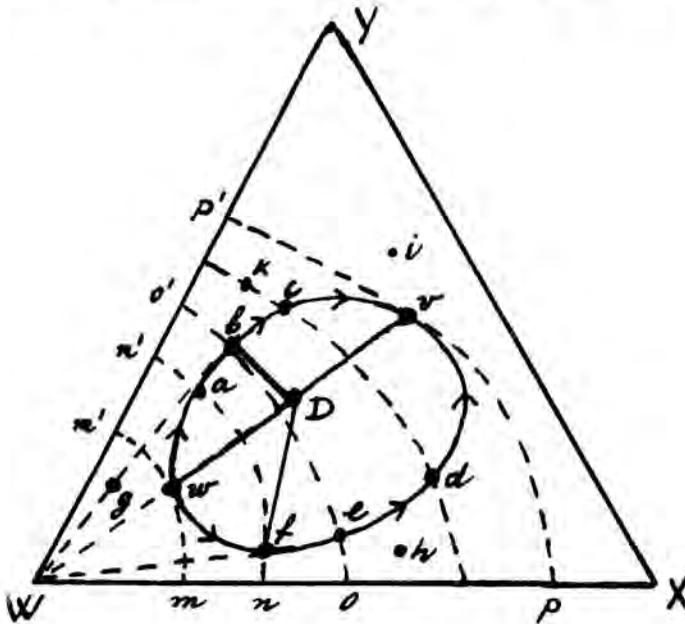


Fig. 2.

Further we shall call  $wbv$  the branch of the saturation-curve rich in  $Y$  and  $wfv$  the branch rich in  $X$ . The dotted curves  $mm'$ ,  $nn'$ , etc. are isotonic curves.

We now easily may deduce:

1°. An isotonic curve intersects the saturation-curve of a ternary compound in two points; the one point of intersection is situated on the branch rich in  $X$ , the other on the branch rich in  $Y$ . The isotonic curves going through  $w$  and  $v$  touch the saturation-curve in  $w$  and  $v$ .

Consequently with each solution of the branch rich in  $X$ , a definite solution of the branch rich in  $Y$  may be in osmotic equilibrium; f. i.  $L_a$  with  $L_f$ ,  $L_b$  with  $L_e$ ,  $L_c$  with  $L_d$  etc.

2°. The *O.W.A.* of a liquid of the saturation-curve is greater (smaller) the more it is situated further from (closer to) the point  $w$ .

Consequently the *O.W.A.* increases on both branches of the curve in the direction of the arrows.

3°. For an isotonic curve and the saturation-curve of a ternary substance in the vicinity of their point of intersection the same is true as for an isotonic curve and the saturation-curve of a component or of a hydrate.

Consequently the curves  $nn'$  and  $oo'$  must touch the lines  $fD$  and  $bD$  in  $f$  and  $b$ .

We also may deduce the property, mentioned sub 2°, a. o. in the following way. We represent the composition of  $D$  by:  $a$  Mol  $X + \beta$  Mol  $Y + (1 - a - \beta)$  Mol  $W$ . Then the saturation-curve  $wv$  is defined by:

$$\zeta + (a - x) \frac{\delta\zeta}{\delta x} + (\beta - y) \frac{\delta\zeta}{\delta y} = \zeta_D \quad . . . . . (14)$$

in which  $\zeta_D$  is the  $\zeta$  of the solid substance  $D$ . The *O.W.A.* of a liquid is defined by:

$$\varphi = \zeta - x \frac{\delta\zeta}{\delta x} - y \frac{\delta\zeta}{\delta y} \quad . . . . . (15)$$

It follows from (14):

$$[(a - x)r + (\beta - y)s] dx + [(a - x)s + (\beta - y)t] dy = 0. \quad . (16)$$

From (15) follows, in connection with (16):

$$d\varphi = -(ar + \beta s) dx - (as + \beta t) dy \quad . . . . . (17)$$

We now take a system of coordinates, the pole of which is represented by point  $D$ , the axis by the line  $DW$ . We let the radius vector to turn at increasing value of  $\mu$  in the direction of the hands of a clock, consequently starting from  $w$ , along  $a$ ,  $b$ ,  $c$  towards  $v$  and backwards along  $d$  towards  $w$ . When we put angle  $DWX = \vartheta$  and when we take for the sake of simplicity angle  $XWY = 90^\circ$ , then we have:

$$\begin{aligned} a - x &= \rho \cos(\mu - \vartheta) & \beta - y &= -\rho \sin(\mu - \vartheta) \\ dx &= \rho \sin(\mu - \vartheta) \cdot d\mu - \cos(\mu - \vartheta) \delta\rho \\ dy &= \rho \cos(\mu - \vartheta) \cdot d\mu + \sin(\mu - \vartheta) \cdot \delta\rho \end{aligned}$$

Substituting those values in (16) and (17) and putting  $\mu - \vartheta = \mu'$ , then we find;

$$\rho [(r - t) \sin \mu' \cos \mu' + s (\cos^2 \mu' - \sin^2 \mu')] d\mu = \dots \quad (18)$$

$$= [r \cos^2 \mu' - 2s \sin \mu' \cos \mu' + t \sin^2 \mu'] \delta \varrho \quad (18)$$

$$d\varphi = -\rho [R \sin \mu' + S \cos \mu'] d\mu + [R \cos \mu' - S \sin \mu'] d\varrho \quad (19)$$

in which:

$$R = ar + \beta s \quad \text{and} \quad S = as + \beta t$$

From (18) again follows the same as is deduced from (5). When we eliminate  $d\varrho$  from (18) and (19) and when we substitute again  $\mu'$  by  $\mu - \vartheta$ , then follows:

$$\frac{d\varphi}{d\mu} = \frac{\rho (rt - s^2) [\alpha \sin (\mu - \vartheta) + \beta \cos (\mu - \vartheta)]}{A} \quad (20)$$

in which  $A$  represents the coefficient of  $d\varrho$  from (18). As further:

$$\frac{\beta}{\alpha} = \text{tg } \vartheta. \quad (21)$$

(20) passes into:

$$\frac{d\varphi}{d\mu} = \frac{-\rho (rt - s^2) \alpha \sin \mu}{A} \quad (22)$$

Consequently  $\varphi$  is maximum or minimum for  $\sin \mu = 0$ , therefore when  $\mu = 0^\circ$  and  $\mu = 180^\circ$ , consequently in  $w$  and  $v$ . For points on branch  $w b v$   $\sin \mu$  is positive and therefore  $\varphi$  decreases starting from  $w$  towards  $v$ ; for points on branch  $v e w$   $\sin \mu$  is negative and consequently  $\varphi$  increases from  $v$  towards  $w$  or reversally it decreases from  $w$  towards  $v$ . As the *O.W.A.* of a liquid increases with decreasing values of  $\varphi$ , the property mentioned sub 2<sup>o</sup> follows from this.

With the aid of fig. 2 the reader now may deduce several properties; briefly we shall discuss a single one.

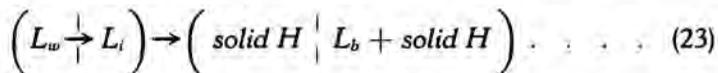
We bring into osmotic contact  $L_w$  with a liquid  $L_q$ .

1<sup>o</sup>. when  $L_q$  is situated within the region  $W m w m'$ , then water diffuses from  $L_q$  to  $L_w$ ;  $L_w$  passes into an unsaturated liquid between  $w$  and  $W$ .

2<sup>o</sup>. when  $L_q$  is situated on the osmotic curve  $m w m'$ , then nothing happens.

3<sup>o</sup>. when  $L_q$  is situated outside the region  $W m w m'$ , then water diffuses from  $L_w$  to  $L_q$ ; then  $L_w$  separates solid  $D$  and dries up totally or partially.

When a complex of  $L_w$  and  $L_i$  is represented f.i. by a point of  $bD$ , then we have the inversion:



Here we have to mean by the *O.W.A.* of the ternary compound the

O.W.A. of the liquid  $L_w$ . Consequently curve  $mwm'$  is the curve (O.W.A. =  $D$ ). We now find:

1<sup>o</sup>. a ternary compound  $D$ , in osmotic contact with a liquid within the region  $Wmwm'$ , removes water from this liquid, with formation of  $L_w + D$  or an unsaturated solution between  $w$  and  $W$ .

2<sup>o</sup>. a ternary compound  $D$ , in osmotic contact with a liquid out of the region  $Wmwm'$ , does not remove water from this liquid.

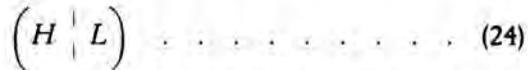
Consequently when we bring into osmotic contact solid  $D$  with a liquid  $L_q$  (fig. 2) then water diffuses to the solid substance. When we bring into osmotic contact solid  $D$  with one of the liquids  $b, v, d, h, k$  or  $i$ , then nothing happens. When, however, we bring into osmotic contact one of those liquids with  $L_w$ , then  $L_w$  is drying up totally or partially with separation of solid  $D$ .

Finally we still have to consider the occurrence of a binary compound between the components  $X$  and  $Y$ . As, however, the results are in accordance with the now mentioned, we shall not discuss this case.

We have assumed with our considerations that water may diffuse from a liquid through a membrane towards other liquids and solid substances. Till now, we have supposed, however, that water can not diffuse through the membrane from solid hydrous substances (f. i. from the hydrate  $H$  in fig. 1 or the hydrous compound  $D$  in fig. 2). In many cases this is surely possible; we shall refer to this later.

When we assume this now, then some deductions must be changed in connection with the O.W.A. of the hydrate  $H$  (and compound  $D$ ).

Let us take the osmotic system



When a little water diffuses from  $H$  to  $L$  then  $H$  passes into  $L_v$  (fig. 1) with loss of water; on the left side of the membrane then arises  $H + L_v$ ; consequently system (24) passes into:



Therefore, it now depends on the O.W.A. of  $L_v$  with respect to that of  $L$ , which shall happen. When  $L$  is situated in the region  $v o X Y$  then  $L$  has a greater O.W.A. than  $L_v$ ; consequently water diffuses from  $L_v$  to  $L$ . As  $L_v$  should become unsaturated then,  $H$  is dissolving, so that the quantity of  $H$  decreases. When  $H$  has totally disappeared, before  $L$  has reached curve  $ov$ , then on the left side a liquid unsaturated and poor in water arises (viz. between  $v$  and  $Y$ ).

We have deduced from fig. 1: a hydrate  $H$  in osmotic contact with a liquid  $L$ :

1<sup>o</sup>. removes water and flows away, when  $L$  is situated within the region  $Wwm$ .

2<sup>o</sup>. rests unchanged, when  $L$  is situated within the region  $mXYvdw$ .  
 We now have to replace region  $mXYvdw$  in 2<sup>o</sup>. by the region  $movidw$ ; in that case is also:

3<sup>o</sup>. separates water and flows away when  $L$  is situated within the region  $v oXY$ .

Therefore we can assume that the hydrate  $H$  has two different *O.W.A.*'s viz.

1<sup>o</sup>. the *O.W.A.* of the solution  $L_w$ , saturated and rich in water, which arises when  $H$  takes water.

2<sup>o</sup>. the *O.W.A.* of the solution  $L_v$ , saturated and poor in water, which arises when  $H$  loses water.

When it is necessary to distinguish the two *O.W.A.*, we shall call the second one the maximum or *M—O.W.A.*

We may also apply those considerations to a mixture of solid substances. In general we may say:

the *O.W.A.* of a solid substance or of a mixture of solid substances is that of the new system, which arises by taking water in;

the *M—O.W.A.* is that of the new system, which arises by losing water.

It is evident that only in that case there may be question of a *M—O.W.A.* when one or more of the solid substances contain water.

*Leiden, Lab. of Inorg. Chemistry.*

*(To be continued).*

**Chemistry.** — "Equilibria in systems, in which phases, separated by a semi-permeable membrane" V. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of January 31, 1925).

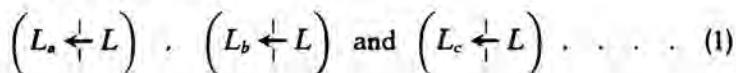
*Ternary equilibria with solid phases.*

After having discussed in the previous communications the occurrence of one solid phase, we now shall consider the case that several solid substances occur.

In fig. 1  $ac$  represents the saturation-curve of  $Y$ ,  $bc$  that of  $X$ ; the dotted curves  $am$ ,  $db$  etc. are isotonic curves; with this is assumed that the *O. W. A.* (osmotic water-attraction) of liquid  $b$  is greater than that of  $a$ . Again the arrows indicate the direction, in which, in accordance with the deductions in previous communications, the *O. W. A.* increases. Hence it appears that the *O. W. A.* of the solution  $c_1$  which is saturated with solid  $X + Y$  is greater than that of all other unsaturated and saturated liquids. The *O. W. A.* of  $L_a$  is equal to that of  $L_m$ , that of  $L_d$  equal to that of  $L_b$ , that of  $L_e$  equal to that of  $L_f$ , etc.

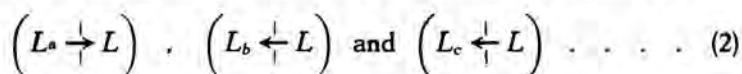
We bring each of the liquids  $a$ ,  $b$  and  $c$  in osmotic contact with an arbitrary liquid  $L$ . In accordance with the situation of  $L$  we find the following.

1°.  $L$  is situated within the region  $Wam$ . The *O. W. A.* of each of the liquids  $L_a$ ,  $L_b$  and  $L_c$  is greater than that of  $L$ ; consequently water diffuses from  $L$  towards the other liquids, which become unsaturated. Consequently we have the osmotic systems:



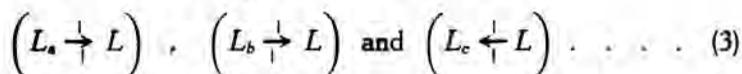
in which the arrows indicate the direction in which the water is diffusing.

2°.  $L$  is situated within the region  $ambd$ . Now the systems are:



Consequently water still diffuses from  $L$  towards  $L_b$  and  $L_c$ , but in contradistinction with sub 1°, from  $L_a$  towards  $L$ .

3°.  $L$  is situated within the region  $bdc$ . We now find:



After the considerations in the previous communications the reader



The water-diffusion in the inverse direction, viz. from the right towards the left, is unlimited also.

In the system  $\left( X + L_c \mid L_c + X + Y \right)$  the water-diffusion from the left towards the right is unlimited also; then at the left side also the substance  $Y$  is deposited. From right to left, however, this diffusion is not unlimited; because if water diffuses towards the left, then  $L_c$  should change its composition along curve  $cb$  starting from  $c$  in the direction towards  $b$  and get, therefore, a smaller *O.W.A.*; consequently the water taken in must diffuse backwards.

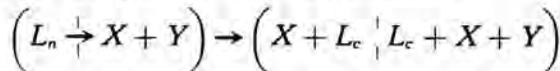
In the system  $\left( X + L_c \mid L_c + Y \right)$  unlimited diffusion is possible in neither direction.

We now bring liquid  $L_n$  (fig. 1) in osmotic contact with a solid mixture  $X + Y$ ; the complex of this mixture is represented by point  $u$ . As the *O.W.A.* of  $X + Y$  is equal to that of  $L_c$ , consequently water shall diffuse from  $L_n$  towards  $L_c$ ;  $L_c$ , however, rests unchanged as long as the two substances  $X$  and  $Y$  remain present. When the point  $u$  has come on the line  $Yc$  by access of water, then  $X$  disappears. With further increase of water the liquid proceeds along the curve  $cd$  and the straight line  $dW$ . As  $L_n$  loses water, this liquid firstly proceeds along the line  $ng$  and afterwards, with deposition of  $X$  curve  $gc$  till in  $c$ . Then the complex is represented by point  $h$ .

It now depends on the ratio, in which we bring together  $L_n$  and the mixture  $X + Y$ , represented by  $u$ , which osmotic equilibrium shall be formed at last. We imagine the complex of  $L_n$  and  $u$  to be represented by a point  $K$  on the line  $nu$  (not drawn). We now may distinguish several cases.

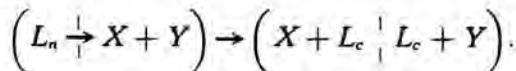
1°.  $K$  is situated on the line  $nu$  within the triangle  $hou$ .

It follows from the previous that the inversion:

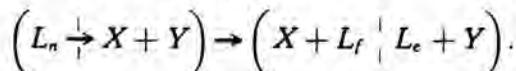


occurs. Consequently  $L_n$  proceeds along the straight line  $ng$  and afterwards along curve  $gc$  till in  $c$ .

2°.  $K$  is the point of intersection of the lines  $nu$  and  $ho$ . We then get the inversion:



3°.  $K$  is situated on the line  $nu$  further from  $u$  than in the case, mentioned sub 2°. We then may get f.i. the inversion:



When we represent the point of intersection of the lines  $Wu$  and  $Ye$  by  $s_1$  and that of the lines  $Wh$  and  $Xf$  by  $s_2$ , then the line  $s_1 s_2$  must go through  $K$ .

Of course it is possible also that the solid substance disappears at one or at both sides of the membrane, so that unsaturated solutions arise.

In fig. 2 we have assumed that, besides the two components  $X$  and  $Y$ , still also the hydrate  $H$  occurs as solid phase;  $ad$  is the saturation-curve of  $H$ ,  $dc$  that of  $Y$  and  $bc$  that of  $X$ . The dotted curves are the isotonic curves; with this is assumed that the  $O. W. A.$  of  $L_b$  is greater than that of  $L_d$ . Again the arrows indicate the direction in which the  $O. W. A.$  increases. It appears from the isotonic curves that the  $O. W. A.$  of  $L_d$  is equal to that of  $L_n$ , that of  $L_c$  equal to that of  $L_b$  and that the  $O. W. A.$  of the liquid  $L_c$ , saturated with  $X + Y$ , is greater than that of all other unsaturated and saturated liquids.

It follows from our previous considerations that the  $O. W. A.$  of the solid substances  $X$ ,  $H$  and the mixture  $X + Y$  is equal to that of the

liquids  $L_b$ ,  $L_a$  and  $L_c$ . We now still have to determine the  $O. W. A.$  of  $Y$ , that of  $Y + H$  and the  $M-O. W. A.$  of  $H$  (see the previous communication).

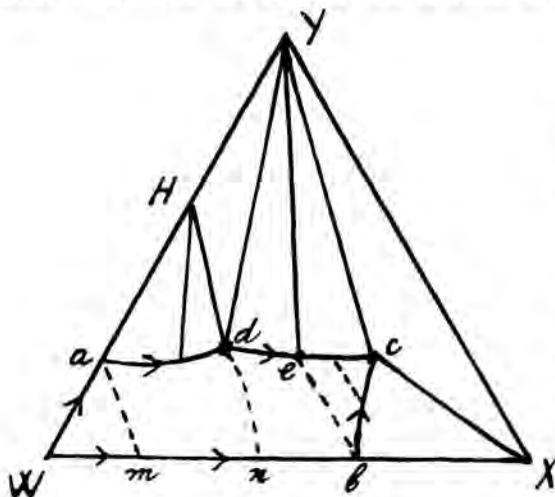


Fig. 2.

When we add a little water to the substance  $Y$ , then is formed an equivalent quantity of  $H$ ; consequently the system  $Y + H$  is formed. When we remove a little water from the hydrate  $H$ , then also the system  $Y + H$  is formed.

The  $O. W. A.$  of  $Y$  and the  $M-O. W. A.$  of  $H$  are, therefore, both equal to that of  $Y + H$ . In order to define the  $O. W. A.$  of  $Y + H$ , we consider the system

$$\left( Y + H \mid L \right) \dots \dots \dots (4)$$

As there is only one liquid, viz.  $L_d$  (fig. 2) which may be in equilibrium with  $Y + H$ , the supposition is obvious that the  $O. W. A.$  of  $Y + H$  shall be equal to that of  $L_d$  and, therefore, also to that of the liquids of the isotonic curve  $nd$ .

We may confirm this in the following way. We represent the composition of:

*H* by:  $\beta \text{ Mol } Y + (1-\beta) \text{ Mol } W$   
*L* by:  $x \text{ Mol } X + y \text{ Mol } Y + (1-x-y) \text{ Mol } W.$

We take  $m, n$  and  $q$  quantities of  $Y, H$  and  $L$ , each with the thermodynamical potential  $\zeta_Y, \zeta_H$  and  $\zeta$ ; we call  $Z$  the total thermodynamical potential of the whole system (4). Consequently we have:

$$dZ = \zeta_Y dm + \zeta_H dn + \zeta dq + q \frac{\partial \zeta}{\partial x} dx + q \frac{\partial \zeta}{\partial y} dy \dots \dots (5)$$

In equilibrium (4) the quantity of  $Y$  rests constant at the left side of the membrane, also the quantities of  $X$  and  $Y$  at the right side and further the total quantity of water. Hence follow the conditions:

$$d(qx) = 0 \quad d(qy) = 0 \quad d(m + n\beta) = 0 \quad d[q + n(1-\beta)] = 0.$$

With the aid of those relations we may write instead of (5):

$$dZ = \left[ \zeta_H - \beta \zeta_Y - (1-\beta) \left( \zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \right) \right] dn \dots \dots (6)$$

When we put:

$$\frac{\zeta_H - \beta \zeta_Y}{1-\beta} = \varphi_1 \quad \text{and} \quad \zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} = \varphi$$

then (6) passes into:

$$dZ = (1-\beta) (\varphi_1 - \varphi) dn \dots \dots \dots (7)$$

It appears from the value of  $\varphi$ , that  $\varphi$  determines the *O. W. A.* of the liquid  $L$ .

In order to find the meaning of  $\varphi_1$  we consider the equilibrium  $H + Y + L_d$  of fig. 2. When we represent the composition of  $L_d$  by  $x_1, y_1$  and  $(1-x_1-y_1)$  then for this are true the equations:

$$\zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} + (\beta - y_1) \frac{\partial \zeta_1}{\partial y_1} = \zeta_H \quad \text{and} \quad \zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} + (1-y_1) \frac{\partial \zeta_1}{\partial y_1} = \zeta_Y.$$

We find from this:

$$\varphi_1 = \frac{\zeta_H - \beta \zeta_Y}{1-\beta} = \zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1}$$

so that  $\varphi_1$  determines the *O. W. A.* of liquid  $L_d$ .

When system (4) is in equilibrium, then  $dZ$  in (7) must be zero, consequently must be

$$\varphi = \varphi_1$$

or: the *O. W. A.* of  $L$  must be equal to that of  $L_d$ ; consequently  $L$  must be situated on the isotonic curve  $nd$ , going through point  $d$  (fig. 2). Consequently it follows from this:

the *O. W. A.* of the substance  $Y$ , that of the mixture  $H + Y$  and the *M-O. W. A.* of the hydrate  $H$  are equal to that of the liquid  $L_d$ , which is in equilibrium with  $H + Y$ .

When  $L$  is situated in the region  $Wn da$  (fig. 2) then is  $\varphi > \varphi_1$ . As only  $dZ$  may be negative,  $dn$  in (7) must, therefore, be positive. This means that the quantity  $H$  in (4) increases, consequently, that water diffuses from the liquid towards the solid substances.

When  $L$  is situated in the region  $ndcb$  (fig. 2) then is  $\varphi < \varphi_1$ . Then it follows from (7) that  $dn$  must be negative, consequently that in (4) water diffuses from the hydrate towards the liquid.

The region  $Wadcb$  (fig. 2) is divided into four parts by the isotonic curves  $am, dn$  and  $be$ . When we bear in mind that:

the O. W. A. of  $H$  is equal to that of the liquids of curve  $am$ ,  
 the O. W. A. of  $H+Y$  and of  $Y$  and the  $M-O$ . W. A. of  $H$  is equal to that of the liquids of curve  $dn$ ,  
 the O. W. A. of  $X$  is equal to that of the liquids of curve  $be$ ,  
 and the O. W. A. of  $X+Y$  is equal to that of the liquid  $c$ ,  
 then we can easily deduce the following:

when we bring into osmotic contact a liquid  $L$  with  $H, H+Y, Y, X$  or  $X+Y$  then:

1°. when  $L$  is situated in the region  $Wam$ , water will diffuse from  $L$  towards those substances;

2°. when  $L$  is situated in the region  $amnd$ ,  $H$  will rest unchanged, but water shall diffuse from  $L$  towards the other substances;

3°. when  $L$  is situated in the field  $dnbe$ , water will diffuse from  $H$  and from  $H+Y$  towards  $L$ ,  $Y$  will rest unchanged and water shall diffuse from  $L$  towards  $X$  and  $X+Y$ ;

4°. when  $L$  is situated in the field  $bec$ , water shall diffuse from  $H$  and from  $H+Y$  towards  $L$ ,  $Y$  and  $X$  shall rest unchanged and water shall diffuse towards  $X+Y$ .

It depends on the situation of the total complex, what will occur on both sides of the membrane, when the osmotic equilibrium is reached.

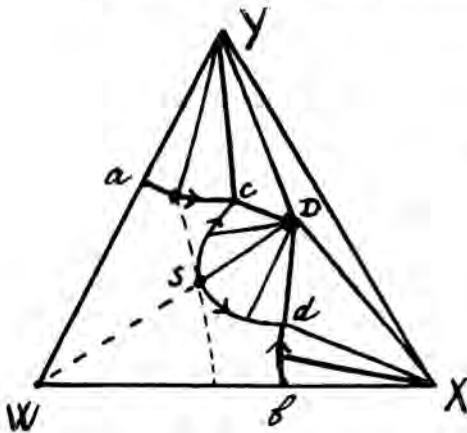


Fig. 3.

soluble without decomposition, in fig. 4 it is decomposed by water with separation of the substance  $X$ .

In figs. 3 and 4 we find, besides the saturation-curves of the two components, still also that of the ternary compound  $D$ . In fig. 3 the point of intersection  $s$  of line  $WD$  and curve  $cd$  is situated on the stable part of the saturation-curve, in fig. 4 on the meta-stable part, which is not drawn. Consequently in fig. 3  $D$  is



changes from point to point; this becomes a maximum when the liquid is congruently saturated, a minimum in the point of solubility of a compound.

We see this proved in the figs. 1—4.

In figs. 1 and 2 the *O. W. A.* increases from *a* towards *c*, becomes a maximum here and decreases from *c* towards *b*, the same is also true for fig. 4.

In fig. 3 the *O. W. A.* increases from *a* till *c*, then it decreases from *c* till *s*, afterwards it increases from *s* till *d* and finally it decreases from *d* to *b*. In *c* and *d* the *O. W. A.* is a maximum, a minimum in *s*.

In the figs. 1—4 we have treated only some of the unnumbered ternary diagrams; with the aid of the considerations in this and the previous communications, the reader, however, will himself be able to examine easily the other cases.

*(To be continued).*

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**Physics.** — “On the Structure of the Ultra-Violet Bands of Water Vapour.” By G. H. DIEKE. (Communicated by Prof. P. EHRENFEST).

(Communicated at the meeting of January 31, 1925).

The so-called ultra-violet emission bands of water vapour have been the subject of an extensive study<sup>1)</sup>. They were formerly ascribed to the H<sub>2</sub>O molecule, or else to oxygen<sup>2)</sup>. WATSON'S<sup>3)</sup> researches, however, rendered it probable that the bands are due to the OH-molecule which is formed in the discharge tube or the flame. Also the structure of the bands pleads in favour of a di-atomic molecule.

After some investigators had arranged part of the lines in series, HEURLINGER<sup>4)</sup> succeeded in arranging almost all the lines of the band  $\lambda$  3064 in twelve branches, which he called  $P_1^k, Q_1^k, R_1^k, P_2^k, Q_2^k, R_2^k$  ( $k=1, 2$ ). This band is the representative of a class of bands, which HEURLINGER calls “bands with doublet-series”. A characteristic of this class is that the lines for small numbers in the series cannot be represented by DESLANDRES'S formula.

The theoretical interpretation of the “H<sub>2</sub>O”-bands, however, presented difficulties<sup>5)</sup>. In contrast with many other bands there are here in one band no combination relations which allow us to isolate the terms. Recently the band  $\lambda$  2811 was measured by WATSON<sup>3)</sup>, who succeeded in showing that its structure is perfectly analogous to the structure of the band  $\lambda$  3064, and that the two bands must belong to the same final state. WATSON found again that the lines themselves do not satisfy the simple theory of band spectra, but that this is more or less the case with the doublet middles.

When use is made of WATSON'S measurements, and these are combined with those of GREBE and HOLTZ<sup>6)</sup> of the band  $\lambda$  3064, it appears possible to get a full insight into the formal structure of these bands without it being necessary to make any supposition concerning the structure of the molecule emitting the bands. The values of all the rotational terms besides a constant — can be calculated, and from the course of the rotational energy as a function of the quantum number  $m$  conclusions can then be drawn concerning the structure of the molecule. In this communication, however, only the formal structure of the bands will be derived and we will not enter into the structure of terms themselves and the conclusions that may be drawn from them.

<sup>1)</sup> Earlier literature in KAYSER, Handbuch der Spectroscopie, Bd. V.

<sup>2)</sup> W. STEUBING, Ann. d. Phys. **33**, p. 553, 1910; **39**, p. 1408, 1912. A. REISS, ZS. f. phys. Chemie **88**, p. 513, 1914.

<sup>3)</sup> W. W. WATSON, Astroph. Journal **60**, p. 145, 1924.

<sup>4)</sup> T. HEURLINGER, Untersuchungen über die Struktur der Bandenspektren, Lund, 1918.

<sup>5)</sup> Compare A. SOMMERFELD, Atombau und Spektrallinien, 3<sup>rd</sup> impr., p. 527.

<sup>6)</sup> L. GREBE und O. HOLTZ, Ann. d. Phys. **39**, p. 1243, 1912.

TABLE I.

m	$Q_1^1(m) - P_1^1(m+1)$		$R_1^1(m) - Q_1^1(m+1)$		$Q_2^1(m) - P_2^1(m+1)$		$R_2^1(m) - Q_2^1(m+1)$	
	$\lambda$ 3064	$\lambda$ 2811						
2	61.36	61.02**	60.94*	61.01	83.61*	83.52*	83.74	83.88
3	101.48*	101.41	101.11*	101.05	117.77	117.90	118.50	118.40
4	140.68*	140.49	140.29	140.14*	152.91	152.60	153.97	153.76
5	178.81	178.87	178.78	178.66*	187.73	187.66	189.62	189.68
6	216.19	216.46*	216.58	216.89	222.70	222.74	225.64	225.18**
7	253.13*	253.11	253.91	254.26*	257.37*	257.76*	261.57*	262.02*
8	288.96*	289.18	290.84	290.43**	292.15**	292.23	297.47*	297.66
9	324.53	324.89*	327.30*	327.23	326.42	326.58	333.28*	333.52*
10	359.38*	359.51	363.22	363.07*	360.20	360.37*	368.87*	368.81
11	393.75	393.76	398.67	398.92	393.87	394.01*	404.10*	404.16
12	427.35	426.72	433.87*	433.78	426.88	427.22	439.30*	439.38*
13	460.41	460.27*	468.24	468.87*	459.38	459.20*	473.24	473.45
14	492.78	493.05	502.14	502.32	491.40	491.65	507.17	506.81*
15	524.46	525.21	535.76*	535.90	522.61	522.90	540.48*	540.78
16	555.43*	555.44	568.27	568.69	553.18	553.33	573.25	573.35
17	585.92	585.85	600.34	600.65*	583.30	583.16	605.43	606.00*
18	615.54	615.40*	631.80	632.48*	612.68	612.31	636.80	637.26
19	644.24	644.15*	662.76	663.38*	640.99	640.77	667.02	668.16
20	672.08	671.73*	692.70*	—	668.70	668.25	697.73	—
21	699.20*	699.62*	722.17	—	695.28	695.92*	727.13	—

m	$Q_1^2(m) - P_1^2(m+1)$		$R_1^2(m) - Q_1^2(m+1)$		$Q_2^2(m) - P_2^2(m+1)$		$R_2^2(m) - Q_2^2(m+1)$	
	$\lambda$ 3064	$\lambda$ 2811						
2	—	58.96	—	—	80.50*	80.58	—	—
3	97.04*	98.17*	—	—	111.09*	114.07*	—	—
4	135.37*	135.08	—	134.51	147.14	146.48**	—	140.20**?
5	171.94	172.05	171.92	172.06	180.96	180.74	—	180.68*?
6	208.09	207.68	208.33*	207.77**	214.34	213.80**	216.78	217.08
7	243.29*	243.74*	243.75	243.68*	247.72	247.53	251.49	252.97**
8	277.82	277.96*	279.48	280.05**	280.72	280.84	285.62	286.34**
9	311.96	311.15*	314.24	—	314.54*	313.74	320.14	—
10	345.48	344.94*	384.73	—	346.66	346.93*	354.73	—
11	378.57	378.21	382.77	—	378.69	—	389.52	—

I. The differences:

$$Q_i^1(m) - P_i^1(m+1) \quad \text{and} \quad R_i^1(m) - Q_i^1(m+1)$$

have within the limits of the errors of observation the same value in  $\lambda 3064$  and  $\lambda 2811$ . (Cf. table I<sup>1)</sup>, i. e.  $Q_i^1(m)$ ,  $P_i^1(m+1)$  and  $R_i^1(m+1)$  must have the same initial state, which we call  $F_i^1(m)$ <sup>2)</sup>. ( $F_i^1(m)$  = energy divided by  $h$ ). We may, therefore, write:

$$\left. \begin{aligned} P_i^1(m) &= F_i^1(m-1) - f_i^P(m) \\ Q_i^1(m) &= F_i^1(m) - f_i^Q(m) \\ R_i^1(m) &= F_i^1(m+1) - f_i^R(m) \end{aligned} \right\} \dots \dots \dots (1)$$

From the fact that

$$Q_i(m) - P_i(m+1) \neq R_i(m) - Q_i(m+1)$$

follows that the equation

$$f_i^P(m) = f_i^Q(m) = f_i^R(m)$$

which is satisfied in a normal band, *cannot* be valid here.

Analogous relations hold for the branches  $P_i^2$ ,  $Q_i^2$ ,  $R_i^2$ <sup>3)</sup>.

II. The six branches  $P_i^1$ ,  $Q_i^1$ ,  $R_i^1$  ( $i=4, 2$ ) form one band (which we shall call I), and the six branches  $P_i^2$ ,  $Q_i^2$ ,  $R_i^2$  another one (II), belonging to another oscillation jump. If, therefore, we ascribe the band  $\lambda 3064$  I to the oscillation transition  $n_1 \rightarrow n_2$ , we obtain the following scheme for the oscillation jumps of the other bands<sup>4)</sup>.

1) In the tables \* denotes that one, \*\* that more than one of the lines, from which the differences have been calculated, coincide with other lines.

2) When judging about the agreement, it should be borne in mind that no importance should be attached to the second decimal. Nor is it impossible that the presence of satellites has affected the accuracy of the measurements.

3) The lines of the branch  $\lambda 3064$  II  $R_2$ , which could not be classified by HEURLINGER, are given by FORTRAT (Journal de phys. 5, p. 20, 1924) according to his new measurements. They do not, however, fit into any of the combination relations following from the structure given here. FORTRAT himself already pointed out that the relation  $R_1 - R_2 = P_1 - P_2 - \delta$  expected by HEURLINGER, is not fulfilled.

If FORTRAT's lines are, however, arranged in the reversed order, then they satisfy all the combination relations within the limits of the errors of observation. For the calculation of the values in the tables I and II this arrangement has been chosen.

It appears from the values with a ? in the tables that the lines  $\lambda = 2876,336$  and  $\lambda = 2875,500$  in the band  $\lambda 2811$  cannot be considered as  $R_2^2(4)$  and  $R_2^2(5)$ .

4) On the assumption that  $n_1 = n_2 = 0$  which is the most probable one the oscillation constants can be calculated from the provisional position of the zero lines. If the oscillation energy according to KRATZER is written  $hn\nu^0(1-nx)$ , one gets

$$\nu_1^0 = 3085.4; \quad \nu_1^0 x_1 = 97.4; \quad \nu_2^0 (1-x_2) = 3569.8.$$

	I.	II.	
$\lambda$ 3064	$n_1 \rightarrow n_2$	$n_1 + 1 \rightarrow n_2 + 1$	(2)
$\lambda$ 2811	$n_1 + 1 \rightarrow n_2$	$n_1 + 2 \rightarrow n_2 + 1$	

That the pieces called I and II of what is called usually a band are in reality two different bands with different oscillation jumps is rendered probable by the fact that the quotient of the term differences in I and II is independent of  $m$ , which is an indication that only the constant  $B$ , which contains the moment of inertia, is different in the term formulae. A direct confirmation of this is obtained with the aid of the combination relations. According to the above scheme  $\lambda$  3064 II and  $\lambda$  2811 I must have the same initial state. Apart from small irregular deviations which must be attributed to errors of observation the differences  $R_i^2(m) - P_i^2(m)$  in  $\lambda$  3064 and  $R_i^1(m) - P_i^1(m)$  in  $\lambda$  2811 now appear actually to have the same values (table II 5<sup>th</sup>–7<sup>th</sup> columns). This confirms, therefore, the scheme of the oscillation transitions, and proves at the same time that:

$$f_i^P(m) = f_i^R(m) = f_i(m).$$

III. When the upper indices are omitted and  $f_i'$  is written instead of  $f_i^Q$ , the six branches of a band are represented by:

$$\begin{array}{ll}
 P_1(m) = F_1(m-1) - f_1(m) & P_2(m) = F_2(m-1) - f_2(m) \\
 Q_1(m) = F_1(m) - f_1'(m) & Q_2(m) = F_2(m) - f_2'(m) \\
 R_1(m) = F_1(m+1) - f_1(m) & R_2(m) = F_2(m+1) - f_2(m)
 \end{array} \quad (3)$$

Now the term-differences, and with them the relative values of the terms can all be calculated. One gets

$$\begin{aligned}
 \Delta F_i(m-1) &= F_i(m+1) - F_i(m-1) = R_i(m) - P_i(m) \\
 \Delta f_i(m) &= f_i(m+2) - f_i(m) = R_i(m) - P_i(m+2) \quad (i=1, 2) \\
 \Delta f_i'(m) &= f_i'(m+2) - f_i'(m) = R_i(m+1) - Q_i(m+2) + Q_i(m) - P_i(m+1)
 \end{aligned}$$

These values are given in the tables II and III.

HEURLINGER already observed that  $R_1(m) - P_1(m)$  and  $R_2(m) - P_2(m)$  differ by a small, about constant amount. This means that the difference between  $F_1(m)$  and  $F_2(m)$  will increase slowly and almost linearly with  $m$ . It is further seen from the tables that the difference between  $f_i(m)$  and  $f_i'(m)$  increases with  $m^2$ , and this may be interpreted as a small difference in the moments of inertia of the molecules in the conditions  $f_i(m)$  and  $f_i'(m)$ .

On the other hand the values of  $f_1$  and  $f_2$  show comparatively great differences for small  $m$ ; they approach each other more and more with increasing  $m$ , which indicates that  $f_1$  and  $f_2$  belong to a different direction of rotation.

The interpretation of the other properties of the terms would necessitate a further discussion of the structure of the molecule, and will therefore be omitted in this communication.

The analogy with the (C + H)-band  $\lambda$  3900, to which HEURLINGER already drew the attention, is corroborated by the combination relations. The same scheme (3) which applies to the bands considered here, was

TABLE II.

$m$	$\Delta F_1(m-1)$ $R_1(m)-P_1(m)$ $\lambda$ 3064 I	$\Delta F_2(m-1)$ $R_2(m)-P_2(m)$ $\lambda$ 3064 I	$\Delta F_1(m-1)$ $R_1(m)-P_1(m)$ $\lambda$ 3064 II	$\Delta F_2(m-1)$ $R_2(m)-P_2(m)$ $\lambda$ 3064 II	$\Delta F_1(m-1)$ $R_1(m)-P_1(m)$ $\lambda$ 2811 I	$\Delta F_2(m-1)$ $R_2(m)-P_2(m)$ $\lambda$ 2811 I	$\Delta F_1(m-1)$ $R_1(m)-P_1(m)$ $\lambda$ 2811 II	$\Delta F_2(m-1)$ $R_2(m)-P_2(m)$ $\lambda$ 2811 II
2	101.44	101.39	—	—	96.66*	96.74	—	—
3	168.94	169.48	—	—	160.75*	160.88	—	—
4	236.35	236.99	—	—	224.60*	225.02	213.51*	205.82**?
5	303.69	304.08	288.87	—	288.47	288.90	273.73	271.92**?
6	370.16	370.70	352.20	352.18	352.02	351.95*	333.71*	333.75
7	436.10	436.78	414.44	414.84	414.90*	415.50*	392.44	394.48**
8	501.80*	501.90**	476.85	476.96	476.59*	477.37	451.51*	451.80*
9	566.27*	566.81**	537.90	537.79	538.04	538.60	—	—
10	630.26	630.69*	598.47	599.11	598.45*	599.12	—	—
11	693.15	693.48*	658.05	659.75	658.51	658.89	—	—
12	755.30*	755.94*	717.13	717.42	717.05	717.90**	—	—
13	815.97	816.40	774.69	—	774.49*	775.27	—	—
14	875.65	876.15	832.66	—	830.72*	830.60**	—	—
15	934.09	934.50*	—	—	886.42*	886.92	—	—
16	991.03	991.53	—	—	940.70*	940.41	—	—
17	1046.81	1047.25	—	—	992.13	992.85*	—	—
18	1100.84	1101.27	—	—	1043.13	1043.26	—	—
19	1153.46	1153.25	—	—	1092.22	1092.39	—	—
20	1204.26	1204.61	—	—	—	—	—	—
21	1253.42	1253.71	—	—	—	—	—	—
22	1300.49	1300.87	—	—	—	—	—	—
23	1346.43	—	—	—	—	—	—	—
24	1389.58*	—	—	—	—	—	—	—
25	1431.01	—	—	—	—	—	—	—

TABLE III.

m	$\Delta f_1(m)$		$\Delta f_2(m)$		$\Delta f_1'(m)$		$\Delta f_2'(m)$	
	$R_1(m) - P_1(m+2)$		$R_2(m) - P_2(m+2)$		$Q_1(m) - P_1(m+1) + R_1(m+1) - Q_1(m+2)$		$Q_2(m) - P_2(m+1) + R_2(m+1) - Q_2(m+2)$	
	$\lambda$ 3064 I	$\lambda$ 2811 I	$\lambda$ 3064 I	$\lambda$ 2811 I	$\lambda$ 3064 I	$\lambda$ 2811 I	$\lambda$ 3064 I	$\lambda$ 2811 I
2	162.42	162.42	201.51	201.78	162.47*	162.07**	201.11	201.92*
3	241.79	241.54	271.47	271.00	241.77*	241.55*	271.74	271.66
4	319.10	319.01*	341.70	341.48	319.46*	319.15*	342.53	342.28
5	394.97	395.12	412.32	412.42	395.39	395.76	413.27	412.84**
6	469.71*	470.00	483.01	482.94*	470.10	470.72**	484.27*	484.76*
7	542.87*	543.44*	553.72	554.25*	543.97*	543.54**	554.84**	555.42*
8	615.37	615.32*	623.89**	624.24	616.26**	616.41	625.43**	625.75*
9	686.68	686.74	693.48**	693.89	687.75	687.96**	695.29*	695.39
10	756.97	756.83*	762.74*	762.82*	758.05*	758.43	764.30*	764.53*
11	826.02	825.71	830.98*	831.38	827.62*	827.54	833.17*	833.39**
12	894.28*	894.05*	898.68*	898.58**	895.59	895.59*	900.12	900.67
13	961.02	961.92**	964.64	965.10	962.55	962.59*	966.55	966.01**
14	1026.60	1027.53*	1029.78	1029.71*	1028.54*	1028.95*	1031.88*	1032.13
15	1091.19	1091.34	1093.66*	1094.11	1092.73	1093.90*	1095.86	1096.25
16	1154.19	1154.54	1156.55	1156.51	1155.77*	1156.09*	1158.61	1158.33*
17	1215.88	1216.05	1218.11	1218.31*	1217.72	1218.33*	1220.10	1220.42
18	1276.04	1276.63	1277.79	1278.03	1278.30	1278.78**	1279.70	1280.47
19	1334.84	1335.11	1335.72	1336.41	1336.94*	—	1338.72	—
20	1391.90	—	1393.31	—	1394.25	—	1395.83	—
21	1447.57	—	1448.68	—	1449.44*	—	1450.83	—
22	1501.25*	—	1502.35	—	1503.67	—	—	—
23	1553.77	—	—	—	1555.69*	—	—	—
24	1603.77	—	—	—	1606.09	—	—	—

found for the  $(C+H)$ -band by KRATZER<sup>1)</sup>. The analogy, however, does not hold for the structure of the terms themselves, which cannot be represented here by KRAMERS and PAULI's formula or by its extension given by KRATZER.

<sup>1)</sup> A. KRATZER, ZS. f. Phys. **23**, p. 298, 1924.

In the  $(C + H)$ -band  $\lambda$  3900 KRATZER assumed terms  $F'_i$  in  $Q_i$ , which might differ somewhat from  $F_i$ . The presence of such terms in the "watervapour bands" is not excluded. No certainty can, however, be obtained on this head from the available observations.

#### Satellites.

HEURLINGER found that some lines are accompanied by satellites, and FORTRAT<sup>1)</sup> proved by new measurements that the presence of satellites is no exception, but the rule in most of the branches. The presence of these satellites may be due to other combinations between the same terms as are also responsible for the main lines. The available measurements, however, do not enable us to come to a positive decision, and it is very well possible that there are still other terms differing little from those found already. Especially in the  $Q$ -branches the matter is very complicated on account of the presence of satellites. If it is tried to use for the derivation only the terms found,  $Q_2$  with its three satellites is e.g. represented by (from red to violet):

$$F_1(m) - f'_2(m); \quad \underline{F_2(m) - f'_2(m)}; \quad F_1(m) - f_2(m); \quad F_2(m) - f_2(m).$$

For not too small  $m$  the last satellite must, however, be further distant from the main line than was observed by FORTRAT, and if the accuracy of the measurements has not been vitiated by the concurrence of several faint lines, this would suggest the presence of another term which may be identical with  $F'_i$  (cf. p. 177). For so far as the accuracy of the measurements admits of a judgment, the satellites of  $P_1$  and  $R_2$  are quantitatively represented by:

$$\sigma P_1 = F_2(m-1) - f_1(m); \quad \sigma R_2 = F_1(m+1) - f_2(m).$$

More extensive measurements of the satellites, also in the band  $\lambda$  2811 will without doubt be able to give information about those particulars of the fine structure of the  $O + H$ -bands, about which so far no certain decision was possible.

Perhaps the circumstance that the " $H_2O$ "-bands were observed by WOOD and his collaborators<sup>2)</sup> in fluorescence, may offer a possibility of arriving at a definite decision by which molecule these bands are emitted. The said investigators found that in nitrogen contaminated by watervapour the " $H_2O$ "-bands appear in fluorescence, but not in dry nitrogen, not when it is contaminated by oxygen either. If WATSON's view, that the bands must be ascribed to the  $OH$ -molecule, is correct,

<sup>1)</sup> R. FORTRAT, Journal de phys. 5, p. 20, 1924.

<sup>2)</sup> R. W. WOOD, Phil. Mag. 20, p. 707, 1910.

R. W. WOOD and G. A. HEMSALECH, Phil. Mag. 27, p. 899, 1914.

C. F. MEYER and R. W. WOOD, Phil. Mag. 30, p. 449, 1915.

the appearance of the bands in fluorescence would have to be explained in this way that excited  $N_2$  molecules, through impacts of the second kind, dissociate an  $H_2O$ -molecule into an excited (or ionized)  $OH$ -molecule and an  $H$ -atom. If so this is not a case of true fluorescence, and in pure sufficiently diluted water-vapour, where impacts of the second kind cannot take place, the fluorescence would, accordingly, have to disappear, whereas it would have to continue to exist if it was due to the  $H_2O$ -molecules.

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**Botany.** — “Conditions influencing the production of colouring matter of *Monascus purpureus* WENT”. By Prof. SHIN-ICHI HIBINO. (Communicated by Prof. F. A. F. C. WENT).

(Communicated at the meeting of March 28, 1924).

Up to the present time, a large number of bacteria and fungi which produce special colouring matter have been described.\* Among these organisms, however, those which have been investigated as to the physiology of the production of colouring matter are very limited in number.

*Monascus purpureus* WENT, which was first described and investigated in detail by WENT (20), is known as producing a characteristic red colouring matter, the chemical nature of which was examined by PRINSEN GEERLIGS (14), who considered it to be an anthraquinon derivative and by BOORSMA (2), who isolated the  $\alpha$ - and  $\beta$ -oryzaerubin components. However, no investigation on the conditions influencing the production of colouring matter has been previously done, and its chemical construction is quite unknown, also.

In former research, special attention was paid to the action of magnesium in the culture medium, for Mg must be considered an essential element for the production of colouring matter in bacteria (THUMM (18), KUNZE (8), BENECKE (1), and SAMKOW (15)), and in fungi (KOSSOWICZ (7), MEDISCH (10) and NAUMANN (13)). In addition to Mg, the importance of phosphorus and sulphur in this respect, was also noticed by some of these investigators, especially by GESSARD (4) and JORDAN (6), who maintained that the essential elements are P and S and that Mg was not essential for the pigment bacteria.

The effect of the sources of nitrogen and carbon and other physical conditions relating to the production of the colouring matter of these organisms were also observed by the above mentioned investigators, as well as by MILBURN (11), SCHKORBATOW (16), SELIBER (17), and others.

So far in the investigations on the production of colouring matter by fungi or bacteria, nothing has been done to compare the quantitative relation between growth and the production of colouring matter although this has great importance in the metabolic physiology of the organisms because of the close connection of the two functions.

In this preliminary note a report is given of the present research, in which this relation was observed, as well as a remarkable effect of Mg, which acts as a stimulant, the effect of carbohydrates as a source of carbon, and other conditions dealing with the production of colouring matter of *Monascus purpureus*; the investigation having been done on material cultured in the Botanical Laboratory in Utrecht.

General description of methods.

As to the methods generally used, special attention is drawn to the following:

**Glassware.** For all the cultures, Jena-glass ERLLENMEYER flasks were used. These were previously boiled with 15% hydrochloric acid for half an hour, then washed carefully with distilled water, prepared by the following method:

**Water.** Water which was used in the preparation of the culture media and for washing glass-ware was distilled in a Jena-glass still.

**Chemicals.** "Chemically pure" chemicals were used. Inorganic chemicals were always recrystallized twice or thrice and in each case even the slightest trace of Mg, SO<sub>4</sub>, and PO<sub>4</sub>, which should be absent in the present experiment, was shown microchemically by the reaction of Mg mixture, BaCl<sub>2</sub>, and Ammonium molybdate mixture.

LINTNER's soluble starch (which I myself made with great care), saccharose, maltose, dextrose, galactose, and lactose showed almost no trace of these three minerals. Fructose, glycogen, inulin, and dextrine, which are naturally very difficult to purify, showed a slight degree of impurity and were used without recrystallization.

**Cotton stoppers.** Special attention was paid to the cotton stoppers, as I realized that during sterilization they give some mineral impurity to the media, therefore the cotton was boiled in 2% HCl, washed with distilled water, and dried.

**Sterilization.** Media were sterilized in the autoclave, under two atmospheres, for half an hour, the subsequent loss of water being corrected by the addition of sterilized water.

**Inoculation.** As *Monascus* produces its spores in the culture medium itself and the mycelium mass is very compact, it is not easy to get spores. Therefore the fungus mass on the surface of a new and vigorous normal culture was cut into fine pieces of as nearly similar size as possible and brought into a flask containing a certain amount of distilled water at 30° C., where they were soaked for one hour to purify them of any substance present. Each piece was then used for inoculation.

**Temperature.** All experiments were carried out in a room of constant temperature of 27° C., the temperature most suitable for this fungus.

**Determination of dry weight of fungus body.** When all other observations had been made, each mass of fungus was isolated from the medium, was carefully washed in water of 45° C., dried at 105° C., and the constant weight determined.

**Determination of colour intensity.** AUTENREATH's colorimeter was used. It is, however, difficult to make the determination accurately, as the purification of the colouring matter of this fungus is not yet possible, for it is really a mixture of various colouring matter, as I shall explain later. Therefore I have taken as standard, in a scale 0—1000, the solution from the maltose culture in which this fungus constantly produced the most intense colour. By this means we can make a relative comparison of the intensity of colour, being supplemented afterwards by the qualitative description. In the present investigation, only the water soluble colouring

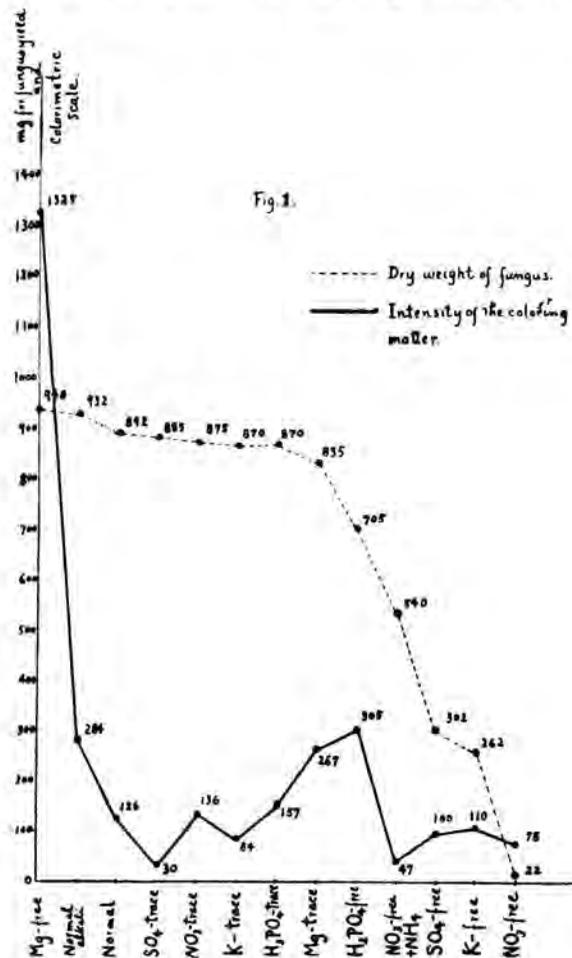
matter was quantitatively observed, the insoluble part being described only qualitatively.

Effects of the essential anions and cations in the culture media upon the production of colouring matter.

The normal culture medium consisted of 3 parts of mineral substances in molecular concentration,  $N/20$   $KNO_3$ ,  $N/100$   $KH_2PO_4$ , and  $N/200$   $MgSO_4$  with 3% of soluble starch, and was found to be very suitable for *Monascus*.

In order to investigate the special action of these two anions, Mg and K, and three cations,  $-H_2PO_4$ ,  $=SO_4$ , and  $-NO_3$ , thirteen groups of culture media were prepared. Each contained the essential anions and cations in the molecular concentration, with the exception of one anion or cation, which, being omitted, was replaced by other salts ("free culture"), or, a certain small amount was added ("trace culture"). In all cases the total concentration of the media was always isomolecular.

Each ERLLENMEYER flask (300 cc.) contained 150 cc. of the medium and 0.5 cc. of  $N/5$  citric acid, with one exception ("normal alkaline"). After ten weeks of cultivation, the following results were observed:



The relation between the production of colouring matter and the essential elements was naturally not similar to that between fungus growth and the essential elements.

Fungus growth was almost normal in the case of the following media: "normal alkaline", "SO<sub>4</sub> trace", "NO<sub>3</sub> trace", "H<sub>2</sub>PO<sub>4</sub> trace", and "Mg trace". It was hindered in "H<sub>2</sub>PO<sub>4</sub> free", and "NH<sub>4</sub> free", still further hindered in "SO<sub>4</sub> free", and "K free", and almost checked in "NO<sub>3</sub> free", as N is needed by the fungus in rather large amounts for plastic substance.

As to the production of colouring matter in the "NO<sub>3</sub> trace", "K trace", and "H<sub>2</sub>PO<sub>4</sub> trace" cultures, and in the "SO<sub>4</sub> free", "K free", and "NO<sub>3</sub> free" cultures, the intensity produced was almost similar to the normal culture. It was a little stronger in the "normal alkaline", "Mg trace", and "PO<sub>4</sub> trace" cultures.

As the source of nitrogen for the growth of the fungus and the production of colouring matter, NH<sub>4</sub> is less favourable than NO<sub>3</sub>.

In the "SO<sub>4</sub> free" culture, the colour of the medium became yellowish.

In general, the mineral constituents of the culture media influence the tone of the colour produced.

It is remarkable that the fungus very intensively produced colouring matter in the "Mg free" culture, while the fungus yield was just the same as in the normal and "Mg trace" cultures. This curious fact causes one to consider that there was still present some small amount of Mg due to the impurity of the chemicals, which were purified, however, with considerable care. This possibility was ascertained by the following experiment.

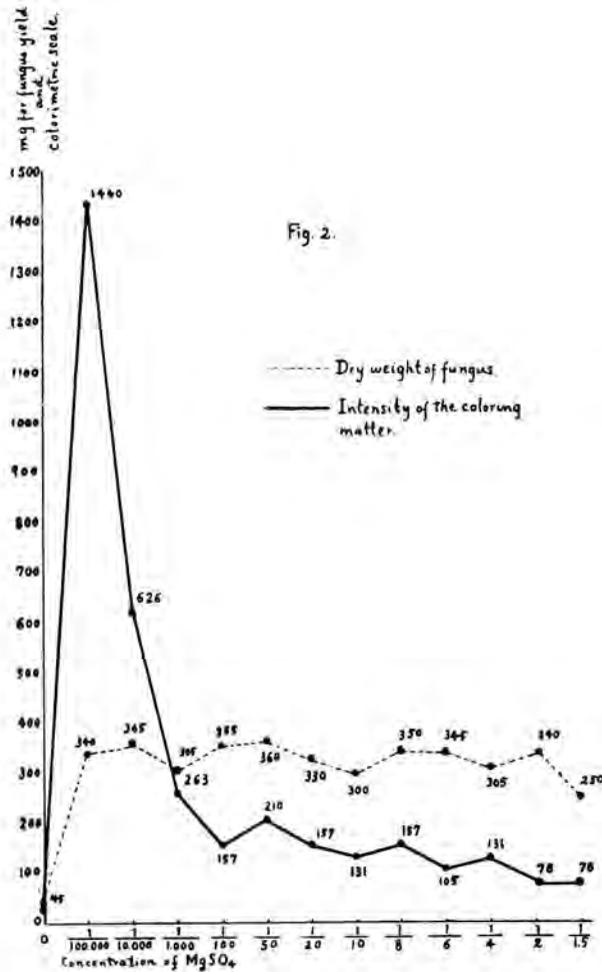
Influence of the various concentrations of Mg.

Culture media containing 0.5% KNO<sub>3</sub>, 0.1% KH<sub>2</sub>PO<sub>4</sub>, and 3% soluble starch or maltose, to which various amounts of MgSO<sub>4</sub> in molecular concentration were added, were inoculated and the results summarized. See fig. 2.

When the Mg concentration was decreased from  $\frac{1}{2} N$  to  $\frac{1}{100,000} N$ , the fungus yield showed almost no difference; the production of colouring matter, however, gradually increased in the descending series, suddenly becoming remarkably intensive in  $\frac{1}{100,000} N$ , but when the Mg concentration is decreased to an infinitesimal degree, neither fungus yield nor production of colouring matter occurred.

In order to leave Mg out of the media absolutely, more careful purification of the chemicals and glass-ware was undertaken, and in addition to the Jena-glass flasks, quartz flasks were used. Under such conditions, a light yield of fungus and a slight production of colouring matter still occurred, while the almost colourless medium showed a light brown tinge. This result assures one that Mg acts as a stimulant in the production of colouring matter of this fungus; one may say it acts almost oligodynamically. It also seems probable that Mg is not a component of this colouring matter and that, although Mg is of course an essential element

(MOLISCH (12), BENECKE (1), LOEW (9), GÜNTHER (5), and others), a certain small quantity is quite sufficient for the growth of the fungus.



#### Influence of the carbohydrates.

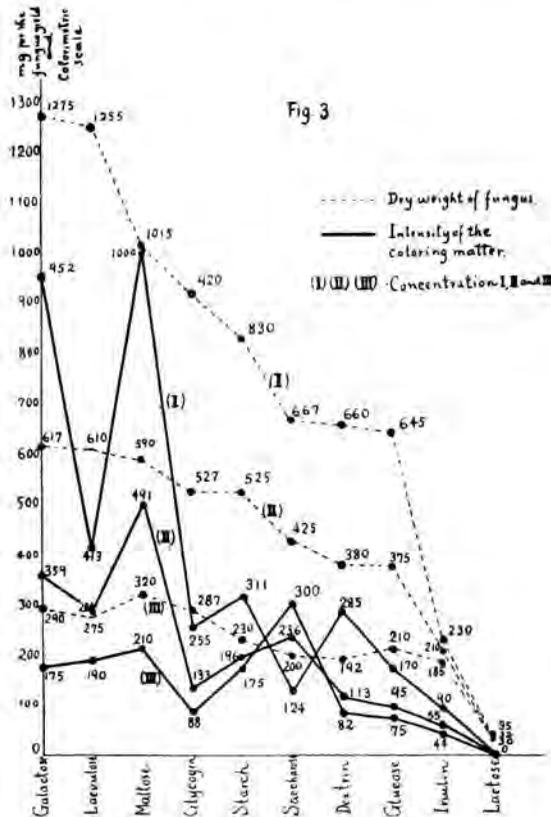
The influence of the carbohydrates, which provide the source of carbon in assimilation and for the production of colouring matter, was investigated. Thirteen sets of culture media were prepared, in which the mineral parts consisted of 0.5%  $KNO_3$ , 0.1%  $KH_2PO_4$ , and 0.01%  $MgSO_4$ , and to which various carbohydrates were added in three different molecular concentrations, as follows:

Concentration I.  $N/2$  for hexoses and polysaccharides and  $N/4$  for disaccharides, the concentration of which is isomolecular to  $N/2$  hexose, when they are completely hydrolyzed by the fungus enzyme.

Concentration II.  $N/4$  was substituted in the above procedure for  $N/2$  and  $N/8$  for  $N/4$ .

Concentration III.  $N/8$  was substituted for  $N/2$  and  $N/16$  for  $N/4$ .

For convenience, in the case of polysaccharides,  $n = 1$ , was taken in the formula  $(C_6H_{10}O_5)_n$ , under the assumption that these substances are absorbed by the fungus only after they have been hydrolyzed into hexoses. Figure 3 shows the results.



Lactose had absolutely no value and inulin was only slightly effective in both assimilation and the production of colouring matter. Their hydrolyzation products, galactose and levulose, were very effective. These results were due to the absence of lactase and inulase in this fungus.

Glucose, dextrose, saccharose, starch, glycogen, maltose, levulose, and galactose were good nutrients for the fungus, but they showed different properties in the production of colouring matter. With maltose and galactose the fungus produced its colouring matter very intensively, while with levulose the intensity was lower, although this hexose gave a large yield of fungus. Saccharose was slowly effective and had a peculiar action for the three different concentrations used, the less concentrated gave the greatest intensity of colour, while the influence of all the other carbohydrates upon the assimilation and the production of colouring matter was rather proportional to their concentrations.

Any of these carbohydrates can be material for the formation of colouring matter, if it is possible for the fungus to assimilate them, though their efficiency in such formation is variable.

In general, contrary to the nature of the mineral constituents in the culture media, carbohydrates do not effect the tone of the colour produced but do influence its intensity.

#### Influence of oxygen.

In the first stage of the growth, when the spores or the mycelium were sunk into the culture medium, either liquid or solid, the colouring matter was not produced. Later, when some mycelium had reached above the surface of the medium, colouring matter was produced just below the surface. This has been observed previously by WENT (20). At a more advanced stage, the colouring matter was produced either in the submerged or aerial parts of the fungus body, if the medium was favourable for growth. Afterwards the medium became stained by the diffusion of colouring matter, while especially the under side of the floating fungus mass was very intensively stained by the colouring matter within the cells.

In the anaerobic culture, the formation of the colouring matter was greatly hindered, thereby differing considerably from the control, while the growth of fungus occurred to some extent. However, I did not succeed in obtaining a perfectly colourless culture. It is, nevertheless, obvious that oxygen is essential for the production of colouring matter.

#### Influence of light.

The production of colouring matter was quite indifferent to the intensity of light. Cultures in the dark and those exposed to the sunlight, both direct and diffused, for the same length of time, showed colour formation and growth of fungus.

#### Influence of temperature.

Temperature had a marked influence upon the production of colouring matter as on the growth of the fungus. The optimum temperature was 27° C.—30° C. Above 35° C. and below 20° C., the production of colouring matter was largely checked.

#### Influence of water content of medium.

The influence of the water content of solid media was observed and some interesting results were found. For instance, a sterilized and coagulated agar-medium, consisting of 0.5%  $\text{KNO}_3$ , 0.1%  $\text{KH}_2\text{PO}_4$ , and 0.01%  $\text{MgSO}_4$ , 3% maltose, and 2% agar, which is very favourable for the production of colouring matter, was cut into several square blocks of different sizes and placed in a sterilized Petri dish. Every block was inoculated at the same time. After a few days, the colouring matter was produced more quickly in the small blocks than in the large ones, according to the differences in the rate of evaporation of the water in the blocks.

Relation between spore formation and the production of colouring matter.

As seen in many cultures under various conditions, the production of colouring matter seemed to follow the formation of spores. It is to be noticed that the colouring matter developed first in the mycelium which produce spores and in the spores, then later in certain mycelium which were rich in reserve material. When colouring matter was intensively produced, the spore formation was also very vigorous. In the culture with lactose medium, in which the fungus remained colourless, spore formation was very slight or lacking altogether.

#### Characteristics of the colouring matter.

According to PRINSEN GEERLIGS (14), the chemical nature of the colouring matter of *Monascus purpureus* was considered to be an anthraquinon derivative, and was described as hardly soluble in water and soluble in ethyl alcohol, chloroform, etc., but this investigator used dried material taken from rough cultures on rice medium, in which 0.1% arsenic acid was used to avoid the propagation of other organisms. BOORSMA (2), in dealing with its solubility in Na hydrate solution, considered that the colouring matter is made up of two components,  $\alpha$ - and  $\beta$ -Oryzaerubin.

Although the present research is not concerned with the chemical nature of the colouring matter, it seems from its physical nature that this colouring matter consists of at least four components, which are produced in both liquid and solid media:

#### a. Water soluble part.

1. Yellow coloured component.
2. Carmine coloured component.

#### b. Water insoluble part, soluble in ethyl alcohol, chloroform, etc.

3. Yellow coloured component.
4. Carmine coloured component.

These four components of the colouring matter seem to be substances closely related chemically, giving fluorescence in their respective solvents.

The proportion of constituents in colouring matter differs according to the environmental conditions; for this reason the tone of the colouring matter varies from yellow to blood red, or carmine, showing various intermediate colours.

It is to be noticed that the colouring matter decreases in solubility when the coloured fungus mass is heated to a temperature above 100° C., or is long dried, so the water soluble part is not obtained. In extracting the Ang-khak mass, some part of the colouring matter which is insoluble in the various solvents always remains. It may be assumed that this was the case in the research of PRINSEN GEERLIGS (14).

For more detailed results, further investigation is necessary.

This research was carried on at the Botanical Laboratory in Utrecht during my visit to Europe.

It is with great appreciation that I thank Professor F. A. F. C. WENT,

who suggested this problem to me and who always helped me with his kind encouragement, as well as putting at my disposal all the facilities of his laboratory.

My thanks are also due to Dr. ANNIE M. HARTSEMA, Mr. S. R. DE BOER, Mr. F. W. WENT, and Miss WILLY M. COELINGH, who often assisted me, and to Mr. P. A. DE BOUTER, who aided me with his mechanical skill.

*Botanical Laboratory.*

*Utrecht, March 1925.*

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**Geology.** — "*On the Direction of the Tertiary Mountain-building Movements in the Island of Java*", by L. RUTTEN.

(Communicated at the meeting of January 31, 1925).

In the year 1917 the Mining-Department in the Dutch East Indies has undertaken a task of pregnant significance for the knowledge of the geology of the Archipelago. In that year namely the first sheet appeared of the geological map on the scale of 1 : 1000.000<sup>1)</sup>. The accompanying preface<sup>2)</sup> informed us, that it was the intention not only to complete this map in 21 sheets, but also to revise the sheets whenever fresh data might be brought forth.

The significance of such maps can be threefold. In the first place, it will often happen that the sketcher detects lacunae in our still very imperfect knowledge of the archipelago, which can be supplied through comparatively little fieldwork. This fieldwork he may then be instructed to execute before finishing the map. Secondly: these maps enable us to note at once the lacunae in our geological knowledge. So for instance BROUWER's map clearly shows the sad state of our knowledge of the islands east of Madura and of the greater part of Sumbawa. Thirdly: such a map may serve as a landmark of our knowledge of the geology of the mapped region; we are thereby enabled to realize at a given moment what conceptions may be derived from the literature. It is true, that this can be attained only if the map is a reliable summary of what is known at a given moment of the region described, and if the designer is well aware that he is a graphical referee of the older literature, and that he should abstain from introducing into the map or into the accompanying profiles his private conceptions, unless they be very carefully thought over. Whereas the first sheet fulfils this condition, it would seem to me that some later sheets do not, and that notably sheet XV (South-Sumatra and West-Java) does not come up to our expectation. The designer, L. J. C. VAN ES<sup>3)</sup> has brought forward in the accompanying text two conceptions which are highly disputable, and which at any rate are not fully verified in the literature: in the first place the author's opinion, that the movements which have folded the tertiary deposits of Java have had a North-South trend, and that this trend is still more pronounced in the structures of the older formations, in the second place

<sup>1)</sup> H. A. BROUWER, Jaarb. Mijnwezen, 44, 1915. Verh. 2, p. 3—48. With map. 1917.

<sup>2)</sup> E. MIDDELBERG. Ibidem p. 1.

<sup>3)</sup> L. J. C. VAN ES, Geol. Overz. kaart van den Nederl. Oost Ind. Archipel, Blad XV. Jaarb. Mijnw. 45, 1916. Verh. 2, p. 55—140, kaart en profielen. 1918.

the author's opinion, that on the basis of our present knowledge of Java and South-Sumatra, a stronger young-miocene folding can generally be distinguished by the side of a less pronounced young pliocene folding.

In the following pages we shall endeavour to ascertain how far the literature justifies the first opinion of VAN ES.

When propounding the question whether the maps and the descriptions by VERBEEK and FENNEMA<sup>1)</sup> furnish some indication of a definite asymmetry — the expression of a definite direction of the folding movements — of the folds of the preneogene strata, it must be answered in the negative. The map of the Bajah-Coalfield (l. c. Map VIII) does not show enough dip-marks, so that nothing definite can be gathered from them; but from the few definite indications they do give, it would seem that the folds of the eocene strata are symmetrical. The map (l. c. VII) of the vicinity of Tjiletu bay seems to indicate symmetrical folding of the schist-formation; however, the surveys are far too little detailed, so that no definite information can be derived from them. The Djiwo-mountains (l. c. VI) are a far too small and too irregularly defined massif to decide on the trend of the folding movement. The largest massif of pretertiary and eocene in Java, the South-Seraju mountains (l. c. V), distinctly illustrates one thing, viz. that the general strike of the pretertiary and the old-tertiary mountains coincides with the present Java-strike<sup>2)</sup>. However, the material available for observation is absolutely insufficient, if we wish to form an opinion about the direction of the folding-movement: in the whole of the pretertiary-eocene territory, measuring  $35 \times 15$  k.m. I see only 15 dip-marks! After VERBEEK and FENNEMA only once a study has been made of the pretertiary strata of Java, viz. by G. NIETHAMMER, who has examined rocks, collected by A. TOBLER in the South-Seraju mountains<sup>3)</sup>. NIETHAMMER pictures a profile through the Loh-Uludistrict, which, according information obtained from Dr. A. TOBLER of Basle, is constructed entirely after the data produced by VERBEEK-FENNEMA, and which marks perfectly symmetrical folding of pretertiary and of tertiary. Finally VAN ES himself speaks — also in accordance with the observations by VERBEEK-FENNEMA — of "a broad-arched anticline" in the Tjiletu-region, "with eocene and miocene wings"<sup>4)</sup>. I do not see how this consorts with the distinctly isoclinal folding of the pretertiary, indicated in his profiles alluded to above.

We, therefore, maintain that the observations in the pretertiary do not at all prove the existence of asymmetrical folding, and that *the intensely isoclinal folding*, which is marked by VAN ES in his profiles (l. c.),

<sup>1)</sup> R. VERBEEK and R. FENNEMA, *Géologie de Java et Madura*. 1896.

<sup>2)</sup> This clashes with the earlier conception of the authors (*Jaarb. Mw.* 1881. I), viz. that the strike of the pretertiary differs from that of the discordant tertiary. This conception, by the way, is no longer adhered to in their map of 1896.

<sup>3)</sup> G. NIETHAMMER. *Tscherm. Miner. Petr. Mitt.* XXVIII, 1909.

<sup>4)</sup> L. J. C. VAN ES. *Jaarb. Mijnw.* 46, 1917. *Verh.* 2, 1919, p. 29.

and which gives the reader, who is not acquainted with the details, an impression of something real, *is not substantiated by known fact.*

The folding in the tertiary requires a more elaborate description. VERBEEK and FENNEMA's work (l. c.) offers but little reliable support, also here. Their profiles are out-of-date; moreover later research has shown that, for obvious reasons, their stratigraphy is at fault on essential points. Still, we wish to point out in the first place that on the profile N<sup>o</sup>. 30, (region to the North of Solo) a very pronounced northward folding is marked, apparently true to nature. Secondly, that on the profile N<sup>o</sup>. 58 through the region South of Radjamandala a northward folding has been indicated — for which region, as will appear later on, VAN ES assumes the reverse, viz. a southward folding. However, it should be observed that the observations of the map do not seem, to warrant the detailed profile of fig. 58.

VAN ES's first publication on the geology of a part of *Bantam*<sup>1)</sup> is accompanied by a map and a profile sheet. With regard to the map the author says (p. 191): "On this map have been marked all the data yielded by the exploration, with the exception of those along the Tji-Liman and the Tji Hara . . . Further we have taken over the strike-, and dip-marks reported by VERBEEK and FENNEMA". It is clear, therefore, that all the details of the profiles must be justified by the observations on the map. Now profile 2 presents an anticline slightly inclined towards the south, which anticline is a continuation of the Bodjong-manik-ant. However, the section does not stand in absolute harmony with the map. The dip-marks on the map are indicative of a rather considerable complexity: in several localities the Mid. Palembang Layers seem to dip away below the Lower Pal. L., and in the profile the chief saddle might even be represented declining southward isoclinally, with a southward isoclinal syncline in the Mid. Pal. Layers, joining up in the North. Neither is the extension of the formations in profile 2 in harmony with the map: on the map along the section line the Lower-Pal.-L. and the Mid-Pal.-L. are about of equal breadth; in the profile the Lower-Pal.-L. are about 2<sup>1</sup>/<sub>2</sub> times broader than the Mid-Pal.-L. Also in profile 4 the Bodjong-manik-anticline is represented inclining slightly towards the south, just as in profile 5. But in profile 4 a steep southern wing is altogether absent on the map, which, to be sure, may be expected to contain all the observations. It is true, a steepness in the southern wing is based on a single observation in profile 5, but all the other observations on the southern wing indicate a flat dip, even flatter than on the northern wing. It may very well be possible, therefore, that the southern steep zone is very narrow — that perhaps the one really observed steep dip has only resulted from a fault — in which case the asymmetry of the anticline would be done away with. At all

<sup>1)</sup> L. J. C. VAN ES. Jaarb. Mijnw. 44, 1915. Verh. 2, 1917.

events the number of observations precludes a decision in this respect. The anticline of Bodjong-manik is taken up again in a publication by ZIEGLER, who busies himself with the Bantam coalfields<sup>1)</sup>. This author maintains on pp. 55—56 that the southern slope of the principal anticline is steeper than the northern one. Of this asymmetry, however, next to nothing is noticeable in ZIEGLER's profiles. (Pl. IV.) Besides these sections are incorrect in different respects. So for instance the slope of the southern wing of the principal anticline in profile 1 is too steep by 7°, the northern wing, on the other hand is not steep enough. In profile 3 the southern wing again is too steep by an average of 15°, while an entirely unwarranted discordance is marked between Lower-Pal.-L. and Mid.-Pal.-L. On this profile the northern wing is also too steep; likewise the southern wing of the anticline on profile 6. So we see, that the anticline of Bodjong-manik does not present in the profiles the asymmetry for which it is credited in the text. Moreover the southern wing is generally too steep. Finally the fitful changes in the strike of the strata in this district suggest a number of unexplained complications, which render the tectonic more intricate. At any rate there is no proof whatever of a southward inclination of the anticline of Bodjong-manik as might be inferred from the pictures of VAN ES and the text of ZIEGLER.

In the second part of ZIEGLER's treatise the eocene coalfields on the south coast of Bantam (the Bajah and the Tji Mandiri field) are discussed. On page 82 we find: "Since the southern wings of the anticlines are generally steeper than the northern, especially in the Tji Mandiri field, we can side with VAN ES in assuming that the push has come from the north". Here again we have to raise some objections: In the profiles of the Bajah-coalfields there is hardly any trace of asymmetry. In profile 2 Pl. V the south wing of the southern anticline is even distinctly less steep than the north wing. Moreover the dips of the south wing are generally overdrawn by 5°. The same applies to the south wing of the most southern anticline in profile 1. On the other hand the slope of the north wing of the most northern anticline in profile 1 is too gentle. If, then, the anticlines in the Bajah-field display a departure from the symmetrical structure, it must be very slight and points rather to an inclination towards the North than towards the South. No more do the profiles of the Tji Mandiri field (Pl. VI) reveal any pronounced push from the North; moreover the maps are only provisional and the condition is very complicated. Only the northern anticline of profile 2 furnishes indications of asymmetry, but here again the northern wing should be drawn steeper. But ZIEGLER's profiles through the Tji Mandiri field induce us to revert to VAN ES's publication of 1918 (Jaarb. 1916), the direct motive for our criticism. As stated above, VAN ES's "Survey-map" is accompanied by a sheet with profiles, which illustrate a southward

<sup>1)</sup> K. ZIEGLER. Jaarb. Mijnw. 47, 1918. Verh. I. 1920.

folding movement. As regards the folding in the tertiary, the most suggestive part is the southern part of profile 5, on which in the eocene two saddles are represented inclining very much towards the South. The text says: "The eocene . . . forms two . . . anticlines, of which the southern wing is much more inclined than the northern". (page 66).

Now, as appears from the place-names, the profile of VAN ES must be situated just between ZIEGLER's profiles I and II through the Tji Mandiri field. We, therefore, considered it well worth, to compare them: in the subjoined diagram the profile of VAN ES is represented between those of ZIEGLER. They are on the same scale. For better comparison I have drawn ZIEGLER's profiles to a greater depth, while sticking faithfully to his interpretation of the facts. It will strike the reader at once that VAN ES's profile does not at all resemble those of ZIEGLER — which have been constructed from a large number of observations. His southern asymmetrical anticline, the south wing of which is, indeed, marked below the sea-level, is to give place to a set of at least 4 steep, symmetrical closely folded saddles<sup>1)</sup>; the more northern, highly asymmetrical syncline of VAN ES is on both profiles of ZIEGLER a fairly symmetrical syncline. Only the most northern anticline of VAN ES is represented asymmetrical with a steep south wing on ZIEGLER's profile II. However, on profile I it is already represented differently, although here an upthrow of miocene, leaning against eocene is represented which, however, is merely a theoretical interpretation. As for profile II we have to point to two facts. In the first place on ZIEGLER's profile at the very least two anticlines are missing (they may indeed be read from his map, but they are absent on the profile). In the second place the anomalous contact between eocene and miocene, as drawn by ZIEGLER, is entirely theoretical, so that the whole saddle might as well have been made symmetrical by drawing the eocene strata on the north wing steeper in the depth and by adding eventually a northward upthrow of the south wing overlapping the north wing. In the third place at *D* ZIEGLER's profile is not at all in keeping with the facts, which point to considerable complication. It may still be pointed out, that the profiles I and II, which are by no means alike, are separated only by three k.m., which is suggestive of strong complication in the lower strata. Only by dint of very detailed work would it be possible to elucidate the tectonic and could an answer be given to the question whether the structures follow a definite trend here.

At all events we feel justified in stating that *the asymmetrical structures as suggested by profile 5 of VAN ES are not supported by any real fact, neither as regards the representation of the tertiary, nor as regards that of the pretertiary.*

<sup>1)</sup> In this profile II near *A* ZIEGLER has drawn one anticline less than has been marked on his map.

ZIEGLER has produced remarkable sections of the Tji-Ditik Leutik, north of the Bajah-field. First of all he gives us of this district (p. 125) a distinct southward upthrust of a coal-layer, but the text (p. 124) gives us the impression that even here the upthrust is not an ascertained fact. <sup>1)</sup>

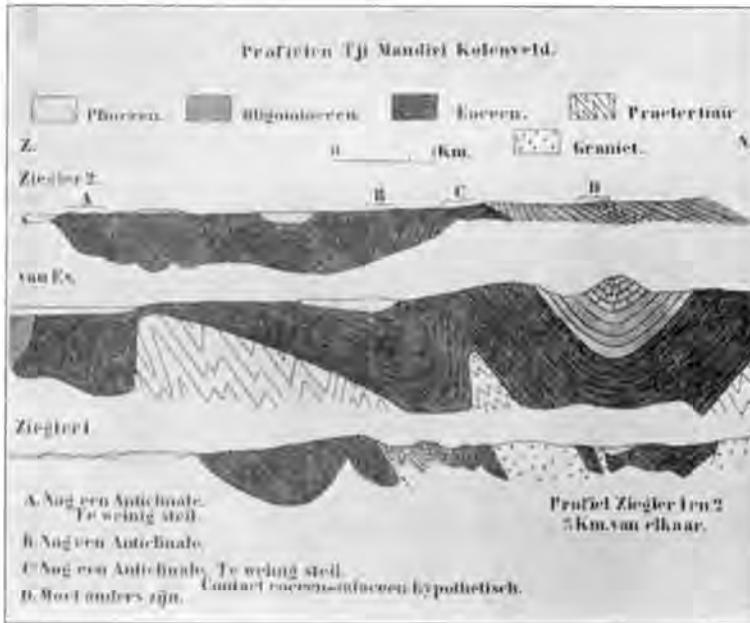


Fig. 1.

The whole upthrust, however, is of no general interest, it regards details only; similar small disturbances will ever occur, howsoever the folding movement may have trended. Of far more essential significance is a profile of some kilometers in length reproduced on p. 125, on which are represented a southwardly inclined syncline with a nucleus of miocene followed in the North by an equally southwardly inclined anticline with an eocene nucleus. This profile *may* be in accordance with the observations on the map, but the text again says: "In fig. 2 . . . . . we have endeavoured to schematize the situation". It appears then that there is some uncertainty also here.

Three things we have to bring into prominence:

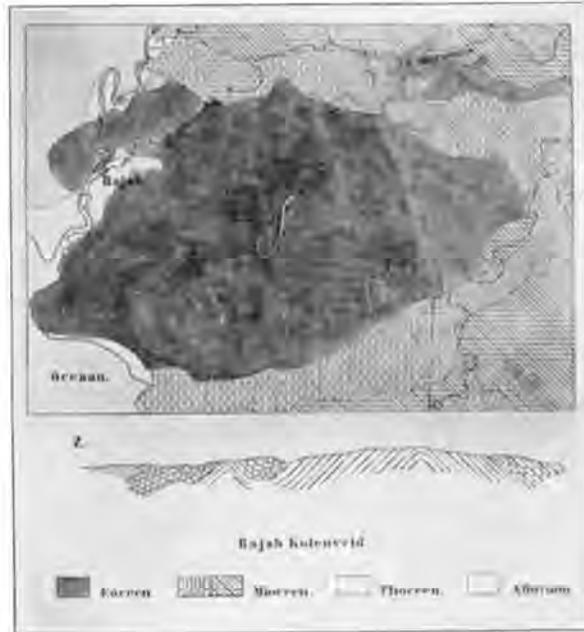
1<sup>o</sup>. that this overfolding, occurring over a small tract, would be an isolated case in a region of symmetrical folds;

2<sup>o</sup>. that this overfolding would occur on the northern wing of a huge anticline, of which the profile is represented perfectly normal only 1 k.m. to the west of the critical point (see fig. 2);

3<sup>o</sup>. that the sketched profile with the twofold overfolding is not only

<sup>1)</sup> "So that presumably we have to do here with a fault".

incompatible with the condition at 1 k.m. to the West, but that also to the East the situation soon changes completely. We see, therefore, that an intense southward push in this region is *not a positive fact*, which ZIEGLER himself admits. With almost equal reason we might apply the



After K. ZIEGLER. 1920.

Fig. 2.

local relations, reported by VAN ES on the northern margin of the anticline of Bodjong-manik (ante p. 193 line 19—15 from the bottom), to prove that in that locality a sharp northward overfolding occurs. Still, this very instance has been mentioned by VAN ES as the most cogent evidence of a southward fold: "Most likely the eocene has been pushed over the more southern oligocene-old miocene orbitoidal limestones of the northern wing of the following anticline" (l.c. 1918 p. 66), and: "However, there are two instances in West-Java which prove distinctly that the first statement (folding-pressure from the North) is correct. These instances are the structure of the most southern anticline near Sukabumi and the anticline of Tji-Djengkol in Bantam (Tji-Ditik Leutic district). It has been *demonstrated* for the first instance by myself, and for the second by ZIEGLER, in the field, that the southern wing has been crushed and that here even an overthrust has occurred in which the pushing force can have come from the North only"<sup>1)</sup> (l.c. 1919 p. 48).

In the treatises by VAN ES of 1918 and 1919 one more instance is

<sup>1)</sup> The marking in brackets and the italics is mine.

mentioned of a saddle in West-Java, which is considered as yielding clear evidence of a southward folding movement. It is the above mentioned anticline to the South of Sukabumi, through which VAN ES has also reproduced a profile (l. c. 1918, northern part profile 3), which is indeed very suggestive (See Fig. 3). The profile runs right over G. Walang, to the South-West of Sukabumi, which is just the „Critical point” in the profile. On closer inspection, however, various objections may be raised also here. In the first place the deeper portion of the profile, which is highly suggestive, and in which again the isoclinally folded pretertiary has been pictured, is purely theoretical. In the second place the surveys on the south wing, which should justify so sharply inclined



After L. VAN ES. 1918.

Fig. 3.

a profile as VAN ES has pictured, have not been carried out, because, according to his own sketch, and also according to the map of VERBEEK-FENNEMA (l. c.) and that by HOOZE<sup>1)</sup> the tertiary is here overlain by volcanic formations and by diluvium. Furthermore, VAN ES's representation does not consort with the data produced by VERBEEK-FENNEMA (l.c.) who mark on the G. WALANG a perpendicular position of the layers. Neither does it consort with those of HOOZE (l. c.), from whose numerous observations — even when making allowance for his still primitive notions of stratigraphy — a section might be constructed far different from that of VAN ES. Now it may very well be the case, that VAN ES has observed facts which account for the northern part of his profile, but when he applies them to set at rest such a problem of principle as the southward folding-movement in the tertiary of Java, he might certainly have stated how far and why the observations of earlier explorers which no doubt are not without relative value, are to be interpreted in a different way. When considering that the excessively overlaid South wing is not verified by observations and that, in accordance with older data, the North wing may look different from VAN ES's section, it is difficult to reasonably conceive an overlaid- to overthrust

<sup>1)</sup> J. HOOZE, Jaarb. Mijnw. 1882. (Scientific section).

saddle. At best we may be safe in maintaining that the anticline of G. Walang possibly possesses a steep zone on the South margin. But let it be remembered in this connection that VERBEEK—FENNEMA (ante p. 193) have sketched some tens of kilometres to the east a profile through the same anticlinal region with a northwardly trended overfolding.

Now when looking once more at the four survey-profiles, recorded by VAN ES in 1918, we are bound to say that N<sup>o</sup>. 4 (Tji-Mandirifield) has lost its suggestive significance, while at the same time the northern portion of profile 3 (G. Walang) cannot afford cogent evidence for a southwardly trended folding. For a single anticline — and that a doubtful one — with a southern steep zone, or even with a southward overfolding does not yet establish a folding movement directed southward<sup>1)</sup>. Profile 1 does not suggest anything, so that only profile 2 and the southern part of the profile 3 are left for discussion. As regards the southern part of profile 3, there is only one locality that implies a slightly southward push, viz. the anticline of Bodjong-Lopang with its steep south limb. I feel inclined to say that also here the condition cannot be quite correct. First of all a steep northward slope occurs on the map of VERBEEK—FENNEMA<sup>2)</sup> also north of Bodjong Lopang, and secondly: in 1912 I visited the vicinity of Bodjong Lopang and found a northward slope of limestones and marlstones in various localities south of the village in the district where according to VAN ES exclusively southward slopes occur. Lastly, as to the profile 2, two remarks have to be made. To the North of Tjipanenga, where a saddle is marked inclining slightly southward, the situation is altogether out of keeping with the map of VERBEEK—FENNEMA and with their profile N<sup>o</sup>. 55, resulting from a number of observations on the map. Between Tjipanenga and Sign. Tjilentab (about the end of VAN ES's profile) VERBEEK and FENNEMA mark three steep, symmetrical anticlines. Here VAN ES's profile presents the peculiar fact of a limestone layer of 300 m. thickness, thinning out completely over a distance of 1 km., which must be considered highly improbable.

Also to the South of Tjipanenga and the North of Pasir Soeren the situation must be more complicated than is indicated by VAN ES, as the surveys of VERBEEK—FENNEMA go to show. In the second place according to VAN ES strata occur to the North of the Tji Odeng in the miocene whose thickness grows up to 300 m. over a distance of not quite 2 km. This again implies that the profile is far from being absolutely

<sup>1)</sup> We are reminded here of many instances in Palembang and Djambi of anticlines with alternating southwesterly and northeasterly steep zone, which alternation may even be traced on one and the same anticline. Or we may compare recent profiles from the Swiss Jura e.g. BUXTORFF Geol. Grenchenbergtunnel, 1917, or ELBER, Verh. Natf. Ges. Basel. 32, 1920.

<sup>2)</sup> To be sure I know that VERBEEK and FENNEMA's map is often deficient, but on the other hand the positive data expressed in the map in the form of dip-marks, are almost always correct.

accurate. This does not preclude the possibility that the anticline of the Tji Mandiri will have a steep south limb.

In his publication of 1919 VAN ES (p. 48) says: "From the shape of the anticlines, of which the south wing is generally steeper than the north wing, we are to conclude that the folding pressure has come from the North". It is impossible, after an examination of the available body of facts, to apply this statement to West-Java for which we rather have to conclude: "*The anticlines in West-Java hitherto known are sometimes broad-arched, sometimes closely folded, but mostly symmetrical. It is probable that there are a few with a steep south wing, but this has not been satisfactorily established for any of them through detailed research. For a determination of a definite direction of the folding movement adequate data are lacking.*"

After having ascertained whether any information may be got about the presence of asymmetrical foldings in the tertiary, from the recent explorations of VAN ES and ZIEGLER, we still have to inquire how far earlier publications on Java can furnish any elucidation on that head. A few years back C. 'T HOEN published<sup>1)</sup> fairly detailed maps and profiles about a tract in North-Rembang. The anticline of Ngandang-Lodan sketched on these maps presents a feeble, though unmistakable overfolding towards the North, and the same may be said of the less known anticline to the West of the G. Butak. It must be added directly that explorations by oil-geologists have brought to light other anticlines in North-Rembang, much more sharply overfolded in a northern direction, but that, on the other hand, there have been detected saddles, that have been intensely overfolded towards the South. Furthermore an anticline has been discovered in the vicinity of Soerabaya, which displays in various localities a northward, in others a southward overfolding.<sup>2)</sup> In a previous paper I have pictured four profiles from the western part of the residence of Soerabaya and more westerly regions<sup>3)</sup> on which the anticlines of Kabuh and Kambangan reveal unquestionable northward overfolding. In addition it may be observed that at the very least on six profiles the presence was established of a steep north limb and a much more horizontal south limb at the anticline of Kambangan. The profile N<sup>o</sup>. 4, via Ngawi, where the folding culminates, and where a folding towards the South would be expected if there were any tendency for it, reveals no indication of such a tendency; there is rather an inclination for northward overfolding. This is the more striking as this profile has been derived from as many as 60 observations, made along the cross-section. Finally broad-arched folding with symmetrical saddle-structure has been recorded from the tertiary region to the North-East of Buitenzorg.<sup>4)</sup>

1) C. 'T HOEN. Jaarb. Mijnw. 45, 1916. Verh. 2, 1918.

2) W. HOTZ u. L. RUTTEN, Zeitschr. f. prakt. Geol. 1915.

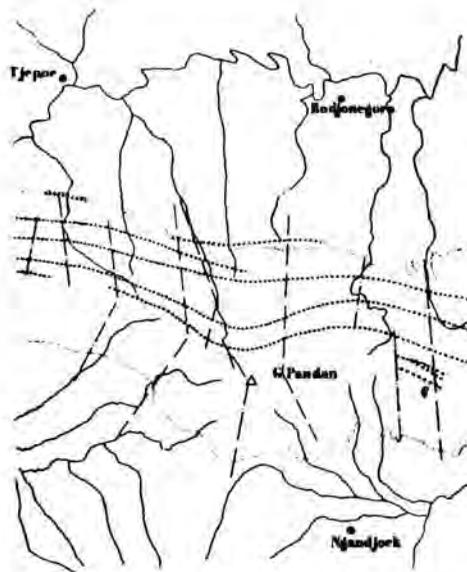
3) L. RUTTEN, Verh. Geol. Mijnb. Gen. Geol. Serie III, 1916.

4) L. RUTTEN, These Proceedings 1917.

In the preceding lines we have passed in review the most important literature concerning Java. We see from it that it contains no indications of a definite direction of the tertiary folding movements. There are indications of a northward movement in East-Java, and a southward movement in West-Java, but they are too feeble to warrant a decision.

However, a few unpublished surveys may still remove the uncertainty. We alluded to it just now that the miocene marl zone, which reaches from Soerabaya as far as the western boundary of Semarang, or perhaps farther, is often characterised by an intense compression, so that if the folding of the Javan tertiary should have had a definite direction, some indication of it might be expected here. It has also been alluded to, that the profile via Ngawi shows a northern trend, small though it may be. Now it appears that the intensity of the folding in the marl-zone increases from East to West. In the year 1912 Dr. W. HOTZ of Basle and myself surveyed a large number of profiles with a view to study the structures. The surveys between the western boundary of Semarang and the meridian of Purwodadi were performed by HOTZ, those to the East of the Solo-river chiefly by myself; three profiles in the neighbourhood of the Pandan-massif were mapped by us in cooperation. Some of these profiles have already been published previously (HOTZ-RUTTEN l.c., RUTTEN l.c., 1916). It may generally be stated here

Anticlinale Assen in het G. Pandan-gebied.



After surveys by W. HOTZ and L. RUTTEN.

++++ Anticlinal axis.

Fig. 4.

that on HOTZ's profiles as well as on mine overfolding towards the North is of much more frequent occurrence than towards the South. Now, there

is a method to ascertain which conclusion the profiles may impart regarding the direction of the folding movements without reproducing the sections, which, indeed, naturally always entail a certain amount of subjective interpretation. With symmetrical folding in E.W. trended mountains the chances of a northward and a southward dip are of course equal. When the overfolding proceeds in a northern direction the chance of finding a southward dip will gradually become greater, until with perfectly isoclinal folding the chance of a southward dip has increased up to 100 %. In case of overfolding towards the South the reverse will take place. The phenomenon will be the more conspicuous as the number of anticlines on a profile increases. On the profiles under consideration this number is rather large. I have counted the observations made by HOTZ and myself separately (together on 30 profiles) to the following effect, the starting number being 100 southward dips:

	Southward dip	Northw. dip
HOTZ	100	60
RUTTEN	100	63

These numbers, relating to more than 800 observations, speak volumes. In the first place they are a striking illustration of the fact that the surveys, which were performed by us separately yield an almost equal percentage of northward dips. *In the second place that the southward dips far outnumber the northern (to the ratio of 100 : 62) which implies a northward folding movement.*

This numerical evidence I conceive to be of vital importance. In addition I wish to add another argument for the northward folding movement in East-Java. The three profiles in the Pandan territory, jointly explored by HOTZ and myself, yielded a curious effect, viz. that to the East of G. Pandan the anticlines tend to bend away towards the South-West whilst to the West of G. Pandan, they curve northward, then again resume their normal direction (approximately E.-W., with a slight departure towards the North). It must be noted that the anticlines referred to run north of the Pandan massif. It is evidenced by the survey, that, at the time of the folding, the large volcanic mass of the G. Pandan must be admitted to have existed already.

Well then, the situation described is readily explained when conceiving the folding movement to have been directed towards the North, through which the plastic marls to the East and to the West of G. Pandan could shift farther towards the North than the rigid Pandan massif itself and the marls lying in its „shadow”. If the direction of the folding had been southward a far different course of the anticlinal axes around the G. Pandan would be expected. *Also the course of the anticlinal axes in the neighbourhood of the Pandan massif favours the hypothesis of the existence of northward folding movements in East-Java.*

It is not expedient to apply this pronouncement to West-Java, where southward movement is not precluded. However, there is something else. According to TOBLER the direction of the folding movement in Sumatra has been from S.-W. to N.-E., from the Indian Ocean to the old Sunda-continent. This hypothesis is based on the fact that in large tracts of Djambi and in adjacent regions the pretertiary strata have been folded distinctly isoclinally with S.-W. dips <sup>1)</sup>. This hypothesis can hardly be contended, although this does not mean to say that we have to *adopt unreservedly* TOBLER's views <sup>2)</sup> as regards a structure of overthrust-sheets in Djambi. If it should appear now that the folding in Central and East-Java points to the same direction of movement — towards Sundaland — as that in Central Sumatra, it is very probable that the same direction will have existed along the western and the southern margin of Sundaland, and that it will also exist in West-Java.

In conclusion I wish to call attention to the fact that on SCHÜRMANN's map of Borneo the folding movement of Macassar Strait is represented directed towards Sundaland, although for Java SCHÜRMANN adopts VAN ES's view that the direction was southward there <sup>3)</sup>.

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<sup>1)</sup> A.o. A. TOBLER, Djambi verslag, 1924, p. 439.

<sup>2)</sup> The arguments adduced by VAN ES (l. c. 1919, p. 107) for westward overthrusts in Sumatra, are in my opinion very weak: for one thing the divergence of the Sumatra-coulisses may remind one of normal virgation, and suppose we can imagine an overthrust here, we may just as well construct the trend of it towards the East as towards the West.

<sup>3)</sup> H. SCHÜRMANN, Geol. Rundschau, XIV, 3, 1924.

**Anatomy.** — "*On the existence of a dolichocephalic race of Gorilla*".  
By Prof. L. BOLK.

(Communicated at the meeting of March 28, 1925).

The discovery of a fossilized not fully grown part of an anthropoid skull at Taungs (South Africa), has rightly awakened general interest; moreover whereas the discoverer — Prof. DART of the university of Witwatersrand (Johannesburg) ascribes the found fossil as belonging to an extinct primate group: "Intermediate between living anthropoids and man<sup>1)</sup>).

It would be rather premature, already to judge the biological importance of the found object, on the ground of the very short description given by DART. For this we will have to wait until the promised detailed description is at hand, after the discoverer will have had the opportunity of comparing the infantile skull of the *Australopithecus africanus*, so named by him, with equally old infantile skulls of the still living Anthropomorphs. It is not unlikely that by this comparison the obvious enthusiasm, wherewith the discoverer views his discovery, and of which his conclusions at present clearly manifest, will have to give place to a more composed criticism and objective judgment. It will in no way wrong the great importance of the discovery; more likely it will do justice to its true morphological significance.

The description of the object by DART, and principally the main arguments, which he gives for his opinion viz. that the new form "exhibits an extinct race of apes intermediate between living anthropoids and man" prompts me to give a short description of a skull, through which our knowledge of the present living Gorilla races is extended and through which the judgment of the morphological importance of the *Australopithecus* skull may be more accurate.

The discoverer begins his description by pointing out "that the whole cranium displays *humanoid* rather than anthropoid lineaments. It is markedly dolichocephalic and leptoprosopic". The first — and as regards the skeleton — the most prominent human attribute of the new form, the longheadedness, together with a long and narrow face is stated.

To what extent this attribute of the *Australopithecus* forms an anti-

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<sup>1)</sup> RAYMOND A. DART. *Australopithecus africanus*: The man-ape of South-Africa. Nature, February 7, 1925.

thesis to the present living man-ape, is known to every morphologist, who more especially studies the comparative anatomy of the Anthropoids.

In the critic of the fossilized remains of the *Australopithecus* by KEITH (Nature Febr. 14, 1925), he especially lays stress on this attribute. He writes: "Even if it be admitted that the *Australopithecus* is an anthropoid ape, it is a very remarkable one. It is a true longheaded or dolichocephalic anthropoid — the first so far known".

Seeing that the type of the skull of the *Australopithecus* promises to play an important part in the discussion on the place of this form in the system, I considered it desirable, to draw the attention to the fact, that also among the present living Gorillas, a race is found, which is strongly dolichocephalic and leptoprosopic and shows both these qualities to the same high degree as the fossil of the *Australopithecus*. This race is evidently only few in number.

Amongst the 50 Gorilla skulls in the Anatomical Museum of the University of Amsterdam only one example of this race is present. This skull is conspicuous on account of its outstanding difference from the rest. To what degree this is so, will be seen from what follows.

The skulls present in the above named museum are partly derived from Camerun and partly from the French Congo. The last named group was obtained throughout years by the intercession of the firm TRAMOND in Paris.

Some years ago this firm again informed me that they held at their disposal three skulls for the museum, "dont un d'une forme particulière". I mention this detail in order to show, how strongly the shape of this skull differs from the rest. That its characteristic shape is due to its strongly dolichocephalic and leptoprosopic nature, I immediately noticed on receiving it.

I never till now could execute my intention of giving a description of this object, but the discovery of the dolichocephalic *Australopithecus* prompts me not to wait any longer.

In order to assure an easy comparison, next to the sketch of the dolichocephalic skull a conformable sketch of the skull of a common brachycephalic Gorilla, will be placed.

In fig. 1 the norma verticalis of the dolichocephalic form is sketched, in fig. 2 that of the brachycephalic. The terms dolichocephalic and brachycephalic, are not truly applicable, in that the index cephalicus is not taken in the same way from full grown Gorillas as from man. As regards the greatest breadth of the cranium, this could if need be, be determined in a comparative way with that in man, but the greatest length is not to be determined, because the strongly developed crista occipitalis in the occipital region and the more strongly developed crista supraorbitalis in the frontal region, make an accurate measurement of the true length of the skull impossible.

Only in infantile skulls, where the crista occipitalis is wanting, the

orbits still situated subcerebral<sup>1)</sup> and the frontal eminence still absent, it is possible to determine an index cephalicus.

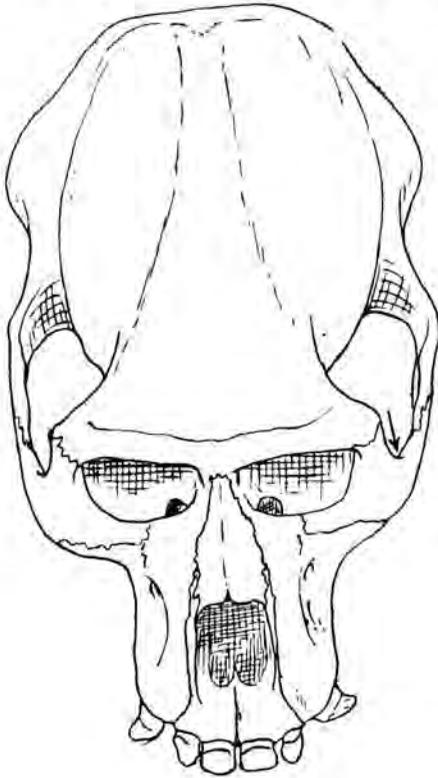


Fig. 1.

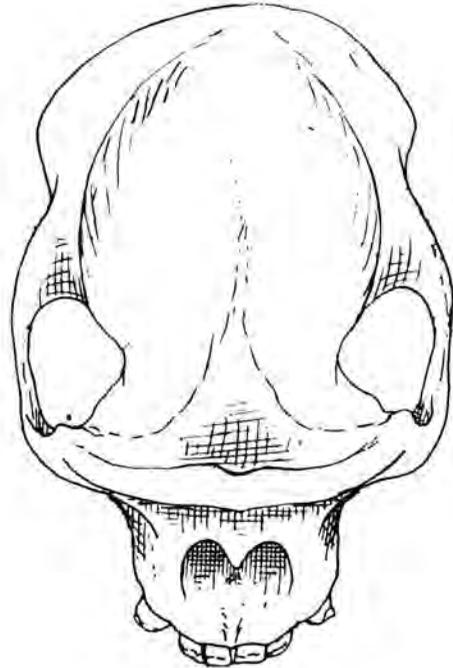


Fig. 2.

In the adult skull the index encephalicus i. e. the length-breadth-relation of the cranial cavity, which is easily to be determined in a sagittal section of the skull, should be used instead of the index cephalicus.

Although the difference in type between the skulls in figs. 1 and 2 is not to be expressed by the value of the index cephalicus, a comparison between both figures leaves no doubt about the essential difference in shape. Both skulls have been drawn, with the arcus zygomaticus running horizontally.

It is immediately evident, that together with the long, narrow cranium of the one specimen, we also find a long and narrow face, while the other object not only has a short round skull, but is also characterized by a short broad face. To this harmonical relation between the shape of cranium and face, the concurrency of dolichocephaly and leptoprosopy, which was also established in the *Australopithecus* by DART, this author especially draws attention to.

<sup>1)</sup> As regards the origin of the supraorbital cristae, the result of the forward shifting of the orbits, see my communication about the significance of the frontal ridges in the Primates. These Proceedings 25, 1922.

We will now study the facial part of the skull more closely. The leptoprosopy in the dolichocephalic Gorilla is the result of two causes, which is easily pointed out by the comparison of figs. 3 and 4. It

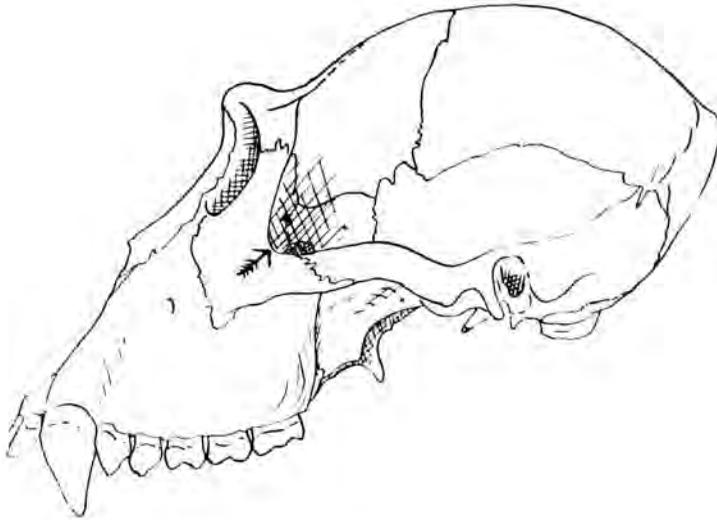


Fig. 3.

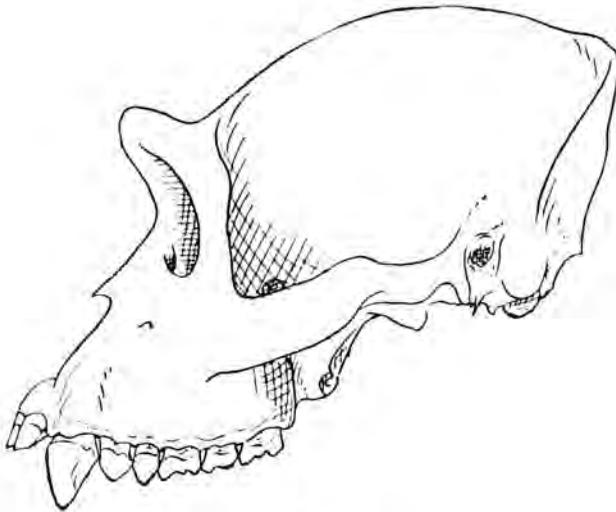


Fig. 4.

follows from measurements, that a true lengthening of the face has taken place. But this cause — about which presently more — is not the only. The leptoprosopy was partly brought about because the base of the face — the palate therefore — was as a whole, pushed horizontally in a frontal direction. This appears to be so, on account

of different anatomical peculiarities, but is most clearly demonstrated by drawing a line perpendicularly down from the highest point of the crista supra-orbitalis. In the brachycephalic skull, this line passes through the row of teeth viz. through 1<sup>st</sup> molar. In the dolichocephalic skull, however, the whole row of teeth lies in front of this line.

As a result of this displacement of the bottom of the face, the facial part of the skull is stretched in length, and has thus acquired a profile, which strongly differs from that of the ordinary Gorilla skull.

The same cause is also to some extent responsible for the difference in the direction of the plane of entrance of the orbits. In the common skull, as appears from figs. 2 and 4 this direction is rather vertically. In the dolichocephalic skull, however, the lower margin of the orbits strongly inclines to the front. The forwardly inclined pterygo-maxillary suture in this skull, in opposition to the vertically directed in the chamaeprosopic type, also is the result of the shifting of the facial base forwardly. In conclusion attention is still drawn to the strongly developed lamina externa, of the Pterygoid, through which the fossa pterygoidea is shaped into a form strongly resembling that of the human skull. I lay stress upon these points because, as said, the skull of *Australopithecus* also is leptoprosopic. The drawings, however, of this object lead us to suppose that in this case the leptoprosopy is caused in the main by the narrowness of the facial skeleton, for there is nothing to see about a shifting of the palate as is the case in our Gorilla. Therefore the profile of the *Australopithecus* differs strongly from that of the leptoprosopic Gorilla. From a comparison between both, no conclusion may however be drawn, the profile of the fossil having still an infantile character.

That, however, the leptoprosopy in our Gorilla is not only due to the lengthening of the face, but has to a large extent the same cause on which the leptoprosopy of the *Australopithecus* depends, viz. the narrowness of the facial skull, will now be shown.

An impression of the difference between the physiognomic aspect of the common Gorilla skull and that of the dolichocephalic form, is acquired by a comparison of figs. 5 and 6. To get a more precise insight into these differences, it is desirable to take a few measurements, and to compare the resulting facial index of the ordinary skull with that of the long headed variety. When one intends to use measurements and indices in order to point out individual differences in the Gorilla, it is not possible to apply the usual measurements of the craniometric system of the human skull. This system has originated in accordance with the shape and structural properties of this skull. The strongly different Gorilla skull, however, requires an own craniometric system. This has already appeared to be so in the index cephalicus, which in the Gorilla cannot be determined in the same way as in man. In the Gorilla, an exact consideration is also necessary to find the appropriate measurements

and method through which the individual differences may be stated accurately by numbers and numerical relations.

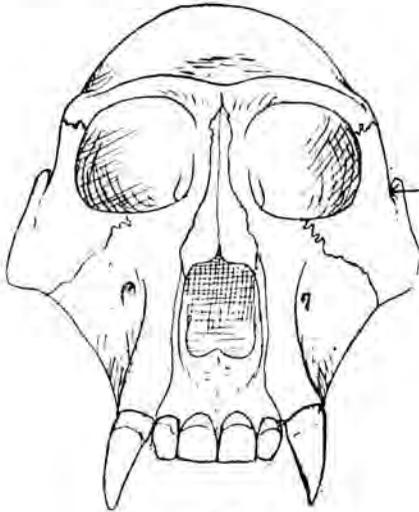


Fig. 5.

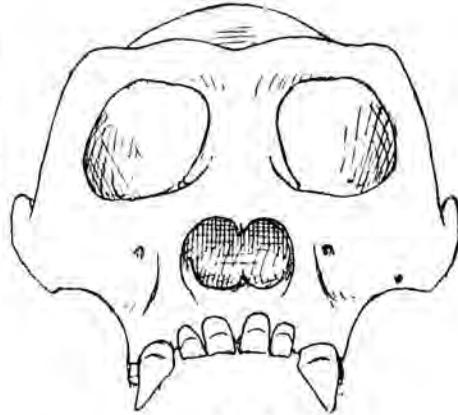


Fig. 6.

As regards the facial skeleton, both the following measurements appear to me the most recommendable to express the facial index. The greatest breadth is taken between the points where the upper margin of the zygomatic arch bends itself round into the lateral orbital margin. This point is represented by a little arrow in figs. 1, 3 and 5. As the greatest length we may take that of the profile, i.e. the distance measured in the median line between the highest point of the *Crista orbitalis* and the front margin of the intermaxillare between the median incisors.

I have determined the length and breadth of the face of 43 adult Gorilla skulls in this way and calculated the index facialis according to the formula  $\frac{100B}{L} = \text{index facialis}$ .

That in the dolichocephalic Gorilla, we indeed have to deal with a separate race, appears convincingly from the fact that with no exception the width of the face of the common Gorilla is greater than its length. The index facialis is therefore always greater than 100. In the dolichocephalic skull, however, the relation is vice versa, the breadth — 120 m.M. is considerably less than the length — 134 m.M. The index facialis is therefore less than 100.

In this short communication it is superfluous to state, in extenso, the measures and the resulting indices of the measured skulls. It is sufficient if I give the general result of my measurements. While the index facialis of the dolichocephalic Gorilla is 89.5, it varied between 103.4 and 122.6 with an average of 111.5 in the common type.

The index facialis of the dolichocephalic skull is therefore much below the variability of the common type. The dolichocephalic skull is therefore not an extreme individual variation of this type, but a true variant of the species with a specific attribute, f.i. a marked leptoprosopy.

As regards the absolute measures it is to be noticed that in the chamaeprosopic type individuals occurred, whose facial breadth was less than that of the leptoprosopic specimen, but they were small female individuals. On the other hand again, some very large skulls, of which the absolute length surpassed that of the leptoprosopic form, are present in the collection. This will become evident from what follows. The face of the leptoprosopic skull was 120 m.M. across and 134 m.M. long. The common skulls varied from 116—170 m.M. across, with an average of 146 m.M., and the length between 101 and 154 m.M. with an average of 131 m.M.

From these figures it now clearly appears, that the leptoprosopy of the dolichocephalic skull is not only due to an increase in the length of the face as a result of the shifting already treated, but also in account of a decrease in the breadth. Because whereas the length is only a little more than the average length of the common skulls i. e. 134:131 m.M., the breadth is considerably less i. e. — 120:146 m.M.

The narrowness of the face is no primary structural property of the skull, it is an adaptation to the dolichocephalic nature of its brain-case because a smaller crane necessarily has a smaller base, also in its forepart, to which the facial part is affixed. Dolichocephaly therefore is the primary and leptoprosopy is the secondary consequence of it, through which the harmonical shape of the whole skull is brought about. The narrowness of the face is associated with the somewhat deviating shape of the orbits from the ordinary. Just as in the *Australopithecus* they are less angled. And as a further harmonic association the entrance to the nasal cavity is long and narrow. These and still other details are clearly seen by a comparison of figs. 5 and 6.

It was evident, that in accordance with the narrowness of the maxillo-orbital part of the face and the base of the skull, the mandible would also be narrower. The comparative investigation has shown this to be so. In this comparison the greatest breadth of the mandible was taken as the distance between both the lateral margins of the condyles. This measure is shown as a dotted line in fig. 7. This dimension, at the same time, gives an impression of the breadth of the base of the skull, as it is identical to the greatest breadth between the two *Fossae glenoidales*. The greatest length of the mandible was determined as the distance from the Incision to a line drawn perpendicularly from the middle of the line, joining the posterior margins of the *capitula mandibulae*. This measure is also represented by a dotted line in fig. 7. The index mandibularis was calculated from the obtained measures to the following way:  $\text{length} \div 100 \times \text{breadth}$ . For 41 common skulls this index varied between

82.7 and 103.3, while it was 71.6 in the mandible of the dolichocephalic skull. There is therefore again a great difference between the relative smallest mandible of the common skulls and those of the particular form, which is a quite apart specimen.

It has already been stated, that it is not possible to determine an index

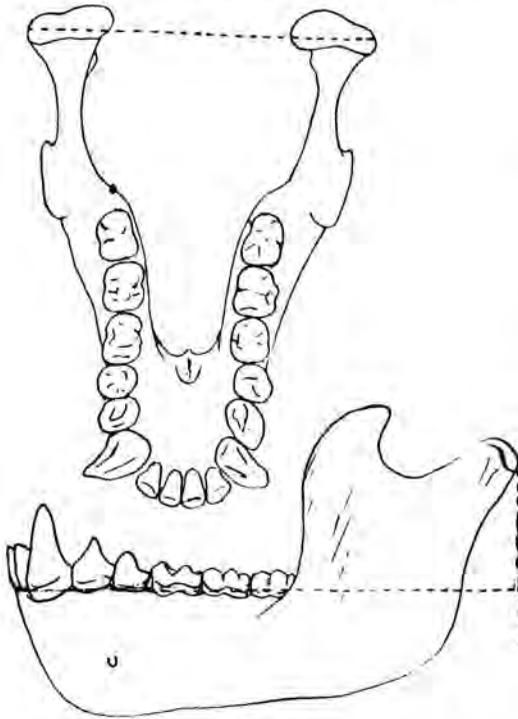


Fig. 7.

communications recommended and applied the Fronton and Occipiton. In literature it is usually wrongly stated that in anthropoids during growth, the frontal part of the braincase is flattened off, through which the frontal vault disappears. This conception is wrong. The vaulting of the frontal region which is externally so clearly seen in the infantile skull of the anthropoids, in reality persists throughout life, but externally this vault is covered, because during the growth the orbits, which originally are situated beneath the brain, even as in man, i.e. beneath the base of the skull are displaced to the front, so that they come to lie anterior to the frontal vault. As a result of this displacement, the orbita receives a new roof, which grows out from the frontal wall of the skull<sup>1)</sup>. One can show this quite easily on a sagittally bisected skull of a full grown Gorilla, the internal surface of the frontal region is not vaulted less in

cephalicus from the adult Gorilla skulls, because during growth the orbits shift themselves in frontal direction, and thus make it impossible to determine the true length of the cranium. The form of the cranium, thus has to be expressed by an index other than the index cephalicus. The most suitable for this is the index encephalicus i.e. the relation between the greatest length and breadth of the cranial cavity. These measurements may be determined quite accurately from skulls sagittally bisected.

As points from which the greatest length of the cranial cavity must be determined, I have in previous com-

<sup>1)</sup> See my communication: Die Topographie der Orbita beim Menschen und Anthropoiden und ihre Bedeutung für die Frage nach der Beziehung zwischen Menschen- und Affenschädel. Verhand. Kon. Akad. v. Wetensch. 2e Sectie, Deel XX. 1919.

such a skull than in an infantile one. Vide f.i. the mediagramms of both the skulls in figs. 8 and 9.

In the mentioned communication the point where the frontal wall and the base of the skull meet in the median line, was termed as Fronton.

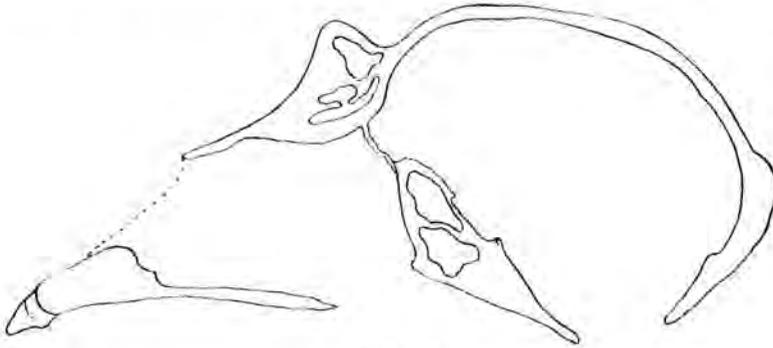


Fig. 8.

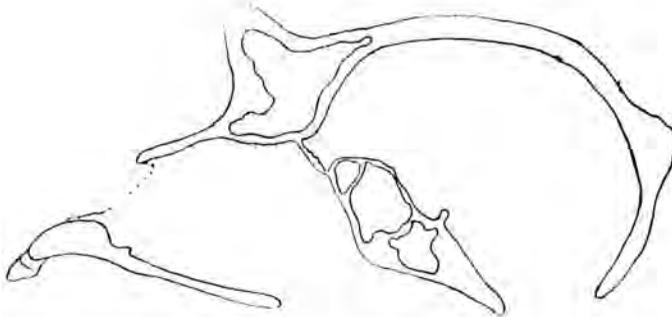


Fig. 9.

As Occipiton was termed the point on the occipital surface of the inner wall most distant from the Fronton. Between both these points is found the greatest length of the cranial cavity. For the greatest breadth add the greatest depth of the cranial cavity of each of the two halves together.

In this way I have determined length and breadth of the cranial cavities in 10 skulls, and calculated the index encephalicus. This varied between 80.6 and 85.9. This therefore confirms the known fact, that the Gorilla is brachycephalic. The index encephalicus of our particular skull again strongly differs from this. The length of the cavum cranii was 127 m.M., the breadth 92 m.M., the index therefore was 72.4.

This index only differs to a small extent from that which KEITH determined for the *Australopithecus africanus*, i.e. 71.

As regards the capacity of the dolichocephalic skull the following may be mentioned. The capacity of the anthropoid skulls, which are in the Anatomical Museum of the University of Amsterdam, has been

determined by one of my assistants<sup>1)</sup> and as regards the Gorilla skulls, he got the following results.

*Capacity of the Gorilla-skull:*

	<i>minimum</i>	<i>maximum</i>	<i>average</i>	<i>number</i>
male	450 c.M. <sup>3</sup>	655 c.M. <sup>3</sup>	550 c.M. <sup>3</sup>	27
female	390 c.M. <sup>3</sup>	595 c.M. <sup>3</sup>	478 c.M. <sup>3</sup>	12

KEITH estimates in his mentioned article on the skull of the Australopithecus the average for the Gorilla skull as 470 c.M.<sup>3</sup> with a maximum capacity of 620 c.M.<sup>3</sup>. From the very accurate researches of HAGEDOORN it follows, that this amount is too little, because it is already surpassed by that of the female skulls. The general average will have to be taken as easily 500 c.M.<sup>3</sup>. The found maximum — 655 c.M.<sup>3</sup> — also is higher than that mentioned by KEITH<sup>2)</sup> i.e. 620 c.M.<sup>3</sup>. The dolichocephalic skull had a capacity which agreed with the average for male skulls i.e. 550 c.M.<sup>3</sup>.

In conclusion mention is still made of the following peculiarity of our skull. The determination of the sex in the common type of skull is quite easy, at least when it concerns adult individuals. The mighty developed and strongly projecting canines, together with the often enormous cristae on the skull, are always a true indication of the masculine skull. As regards the sex of our skull I, however, am undecided. The strongly developed canines will lead to think of a masculine skull, but a crista sagittalis is totally absent, the lineae temporales do not even reach the median line. From this we may conclude, to a mediocre development of the muscoli temporales; the muscoli pterygoidei, on the contrary, appear to have been developed more strongly than in the common Gorilla. DUCKWORTH already remarked<sup>3)</sup> that in the Gorilla as a rule the lamina externa of the Pterygoid is weakly developed, and the Fossa pterygoidea is shallow. In the dolichocephalic Gorilla, this lamina is broad, and the Fossa deep, just as in man. This lesser development of the muscoli temporales and stronger development of the muscoli pterygoidei may perhaps stand in connection with a somewhat varied mechanism of the so much narrower mandible of the dolichocephalic type.

<sup>1)</sup> A. HAGEDOORN. Schedelcapaciteit van Anthropomorphen. Ned. Tijdschr. v. Geneeskunde. Jaargang 1923.

<sup>2)</sup> See also A. KEITH. The Growth of Brain in Men and Monkeys. Journ. of Anat. and Phys. Vol. XXIX. 1895.

<sup>3)</sup> W. L. H. DUCKWORTH. Variations in crania of Gorilla savagei. Journ. of Anat. a. Phys. Vol. XXIX. 1895.

**Mathematics.** — “Ueber projective Differentialinvarianten” III. Von Prof. R. WEITZENBÖCK.

(Communicated at the meeting of January 31, 1925).

In dieser Mitteilung zeige ich, wie man aus den, in der ersten Mitteilung abgeleiteten “Klammerausdrücken” invariante Differentialformen gewinnt. Ferners beweise ich einen Satz über das identische Verschwinden von Klammerausdrücken.

§ 1.

Wenn wir in

$$J = \{ K_1, K_2, \dots, K_{m+2} \} = \begin{vmatrix} q_1 K_1 \dots q_{m-1} K_{m-1} & q_m K_m & q_{m+1} K_{m+1} & q_{m+2} K_{m+2} \\ p_1 K_1 \dots p_{m-1} K_{m-1} & p_m K_m & p_{m+1} K_{m+1} & p_{m+2} K_{m+2} \\ \frac{\partial K_1}{\partial t_1} \dots \frac{\partial K_{m-1}}{\partial t_1} & \frac{\partial K_m}{\partial t_1} & \frac{\partial K_{m+1}}{\partial t_1} & \frac{\partial K_{m+2}}{\partial t_1} \\ \dots & \dots & \dots & \dots \\ \frac{\partial K_1}{\partial t_m} \dots \frac{\partial K_{m-1}}{\partial t_m} & \frac{\partial K_m}{\partial t_m} & \frac{\partial K_{m+1}}{\partial t_m} & \frac{\partial K_{m+2}}{\partial t_m} \end{vmatrix} \dots \quad (1)$$

voraussetzen, dass  $K_1, K_2, \dots, K_{m-1}$  absolute Invarianten sind, dann ist

$$q_1 = q_2 = \dots = q_{m-1} = 0 \quad \text{en} \quad p_1 = p_2 = \dots = p_{m-1} = 0.$$

Fassen wir dann in (1) die drei letzten Kolonnen zusammen, so gibt die Entwicklung nach LAPLACE:

$$J = \sum_i \begin{vmatrix} q_m K_m & q_{m+1} K_{m+1} & q_{m+2} K_{m+2} \\ p_m K_m & p_{m+1} K_{m+1} & p_{m+2} K_{m+2} \\ \frac{\partial K_m}{\partial t_i} & \frac{\partial K_{m+1}}{\partial t_i} & \frac{\partial K_{m+2}}{\partial t_i} \end{vmatrix} \cdot \frac{\partial (K_1, K_2, \dots, K_{m-1})}{\partial (t_1, \dots, t_{i-1}, t_{i+1}, \dots, t_m)} \quad (2)$$

Hier ist der zweite Faktor  $D^i$  gleich der Funktionaldeterminante von  $K_1, K_2, \dots, K_{m-1}$  bezgl. der Veränderlichen  $t_1, t_2, \dots, t_{i-1}, t_{i+1}, \dots, t_m$ . Gegenüber den Parametertransformationen

$$t_i = t_i(\bar{t}_1, \bar{t}_2, \dots, \bar{t}_m) \quad , \quad dt^i = \frac{\partial t_i}{\partial \bar{t}_\mu} d\bar{t}^\mu \dots \quad (3)$$

sind diese Funktionaldeterminanten kogredient mit  $dt^i$ . Denn: ist  $L_m$  eine  $m$ -te absolute Invariante, so haben wir:

$$\bar{D} = \frac{\partial (\bar{K}_1, \bar{K}_2, \dots, \bar{K}_{m-1}, \bar{L}_m)}{\partial (\bar{t}_1, \bar{t}_2, \dots, \bar{t}_m)} = \Delta \cdot \frac{\partial (K_1, K_2, \dots, K_{m-1}, L_m)}{\partial (t_1, t_2, \dots, t_m)} = \Delta \cdot D$$

und wegen

$$D = \sum_i \frac{\partial (K_1, K_2, \dots, K_{m-1})}{\partial (t_1, t_2, \dots, t_{i-1}, t_{i+1}, \dots, t_m)} \cdot \frac{\partial L_m}{\partial t_i} = \sum D^i \cdot \frac{\partial L_m}{\partial t_i}$$

ist also:

$$\begin{aligned} \bar{D} &= \sum_v \bar{D}^v \frac{\partial \bar{L}_m}{\partial t_v} = \sum_v \bar{D}^v \cdot \frac{\partial L}{\partial t_i} \frac{\partial t_i}{\partial t_v} \\ D^i &= \frac{1}{\Delta} \cdot \bar{D}^v \frac{\partial t_i}{\partial t_v} \dots \dots \dots (4) \end{aligned}$$

Wir können also in (2)  $D^i$  statt  $dt^i$  schreiben. Ersetzen wir dann noch  $K_m, K_{m+1}$  und  $K_{m+2}$  durch  $K_1, K_2$  und  $K_3$ , so ergibt sich der Satz:

Sind  $K_1, K_2$  und  $K_3$  drei Invarianten mit den  $\Delta$ -Gewichten  $q_i$  und den  $\lambda$ -Gewichten  $p_i$ , dann ist

$$[K_1, K_2, K_3] = \begin{vmatrix} q_1 K_1 & q_2 K_2 & q_3 K_3 \\ p_1 K_1 & p_2 K_2 & p_3 K_3 \\ dK_1 & dK_2 & dK_3 \end{vmatrix} \dots \dots \dots (5)$$

eine projektiv-invariante Differentialform mit  $\Delta$ -Gewicht  $q_1 + q_2 + q_3$  und mit  $\lambda$ -Gewicht  $p_1 + p_2 + p_3$ .

Wir haben auch:

$$\begin{aligned} [K_1, K_2, K_3] &= \sum dK_1 (q_2 p_3 - q_3 p_2) \cdot K_2 K_3 - K_1 K_2 K_3 \cdot \sum (q_2 p_3 - q_3 p_2) \cdot d(\log K_1) \\ \frac{[K_1, K_2, K_3]}{K_1 K_2 K_3} &= d \log (K_1^{q_2 p_3 - q_3 p_2} K_2^{q_3 p_1 - q_1 p_3} K_3^{q_1 p_2 - q_2 p_1}) \dots \dots (6) \end{aligned}$$

Hieraus folgt z.B., dass  $[K_1, K_2, K_3] = 0$  die Abhängigkeit

$$K_1^{2_1} K_2^{2_2} K_3^{2_3} = const. \dots \dots \dots (7)$$

gibt.

Weiters folgt aus (5) — analog mit den Gleichungen (29), (30) und (31) der ersten Mitteilung — dass die Klammerausdrücke  $[K_1, K_2, K_3]$  die folgenden Relationen erfüllen:

$$[K_1, K_2, K_3 + K_4] = [K_1, K_2, K_3] + [K_1, K_2, K_4] \dots \dots (8)$$

$$[K_1, K_2, K_3 K_4] = [K_1, K_2, K_3] \cdot K_4 + [K_1, K_2, K_4] \cdot K_3 \dots \dots (9)$$

$$\left[ K_1, K_2, \frac{K_3}{K_4} \right] = [K_1, K_2, K_3] K_4^{-1} - [K_1, K_2, K_4] \cdot K_3 K_4^{-2} \dots (10)$$

§ 2.

Nehmen wir jetzt für  $K_1, K_2$  und  $K_3$  die Invarianten

$$U = (u'y) \quad X = (v'x) = (yy_1 \dots y_m x)$$

dann ergibt (5) die beiden Invarianten:

$$[U_1, U_2, X] = \begin{vmatrix} 0 & 0 & (v'x) \\ (u'_1y) & (u'_2y) & (m+1)(v'x) \\ (u'_1dy) & (u'_2dy) & (dv'x) \end{vmatrix} = (v'x) \cdot (\pi'y) (\pi'dy) \cdot (\pi'_{ik} = (u'_1 u'_2)_{ik})$$

und

$$[U, X_1, X_2] = \begin{vmatrix} 0 & (x_1v') & (x_2v') \\ (u'y) & (m+1)(x_1v') & (m+1)(x_2v') \\ (u'dy) & (x_1dv') & (x_2dv') \end{vmatrix} = - (u'y) \cdot (\pi v') (\pi dv') \cdot (\pi_{ik} = (x_1 x_2)_{ik}).$$

Wir erhalten so die beiden mit einander dualen Invarianten:

$$Y = (\pi^m y dy) = m! (\pi'y) (\pi'dy) = m! \sum \pi'_{ik} (y dy)_{ik} \quad . \quad . \quad (11)$$

und

$$V = (\pi'^m v' dv') = m! (\pi v') (\pi dv') = m! \sum \pi_{ik} (v' dv')_{ik} \quad . \quad (12)$$

$Y=0$  gibt die Tangente  $\overline{y dy}$ ;  $V=0$  ist die Gleichung des mit der Tangente bezgl. des Asymptotenkegels konjugierten linearen  $R_{m-1}$ .

$Y$  hat das  $\Delta$ -Gewicht 0 und das  $\lambda$ -Gewicht 2;  $V$  hat das  $\Delta$ -Gewicht 2 und das  $\lambda$ -Gewicht  $2(m+1)$ . Die Ueberschiebung beider gibt Null wegen

$$(v'dy) = - (y dv') = 0 \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Aus  $U, X, Y$  und  $V$  leiten wir weiters ab:

$$R = [X, Y, V] = 2Y [(xv') (\pi'^m v' d^2v') - 2 (x dv') (\pi'^m v' dv')]$$

$$S = [U, Y, V] = 2V (u'y) (\pi^m y d^2y) - 2 (u'dy) (\pi^m y dy);$$

hieraus durch Ueberschiebung:

$$\sum_{ik} \frac{\partial R}{\partial \pi'_{ik}} \cdot \frac{\partial S}{\partial \pi_{ik}} = - 4m! UXYV \cdot F_2^2.$$

wo

$$F_2 = (v' d^2y) = (y d^2v') = - (dy dv') = (y y_1 \dots y_m y_{ik}) dt dt^k \quad . \quad (14)$$

die erste quadratische Differentialform ist. Dadurch ist  $F_2$  und also auch

$$A = |(v' y_{ik})| = |(y y_1 \dots y_m y_{ik})| \quad . \quad . \quad . \quad . \quad (15)$$

gewonnen.  $F_2$  hat das  $\Delta$ -Gewicht 1 und das  $\lambda$ -Gewicht  $m+2$ .

Wir zeigen nun noch, wie auch die kubische Differentialform auf diese Weise erhalten werden kann. Es ist

$$M = [X, F_2, A] = \begin{vmatrix} (xv') & F_2 & (m+2) A \\ (m+1)(xv') & (m+2) F_2 & m(m+2) A \\ (x dv') & dF_2 & dA \end{vmatrix}$$

$$M = (xv') [F_2 \cdot dA + (m+2) A \cdot dF_2] - 2(m+2) (x dv') \cdot A F_2 \quad . \quad (16)$$

$M$  hat das  $\Delta$ -Gewicht  $m + 4$  und das  $\lambda$ -Gewicht  $m^2 + 4m + 3$ . Weiters:

$$N = [U, F_2, A] = \begin{vmatrix} 0 & F_2 & (m+2) A \\ (u'y) & (m+2) F_2 & m(m+2) A \\ (u'dy) & dF_2 & dA \end{vmatrix}$$

$$N = (u'y) \cdot [(m+2) AdF_2 - F_2 dA] - 2(m+2)(u'dy) AF_2. \quad (17)$$

$N$  hat das  $\Delta$ -Gewicht  $m + 3$ , das  $\lambda$ -Gewicht  $m^2 + 3m + 3$ .

Wenn wir nun  $[M, N, A]$  berechnen, so finden wir:

$$[M, N, A] = 12(m+2)^2 \cdot A^2 F_2^2 \cdot F_3. \quad (18)$$

wo

$$F_3 = (m+2) A [3 dF_2 - 2(v'd^2y)] - 3F_2 \cdot dA \quad (19)$$

die gesuchte kubische Differentialform. Sie hat das  $\Delta$ -Gewicht  $m+3$  und das  $\lambda$ -Gewicht  $m^2 + 3m + 2$ .

Die Invariante

$$C = [U, X, A] = \begin{vmatrix} 0 & (xv') & (m+2) A \\ (u'y) & (m+1)(xv') & m(m+2) A \\ (u'dy) & (x dv') & dA \end{vmatrix}$$

oder

$$C = C(x, u') = (m+2) A [(u'y)(x dv') - (u'dy)(xv')] - (u'y)(v'x) \cdot dA \quad (20)$$

ist eine lineare Differentialform und  $C(x, u') = 0$  gibt einen besonderen, mit dem Punkte  $y$  invariant verknüpften, linearen Konnex.

§ 3.

Setzen wir in (1) voraus, das

$$J = \{K_1, K_2, \dots, K_{m+2}\} \equiv 0 \{y\} \quad \text{und} \quad \equiv \equiv \{K\} \dots \quad (21)$$

d.h.  $J$  verschwindet identisch, wenn wir alle  $K_i$  durch die  $y, y_a, y_{\alpha\beta}, \dots$  ausdrücken;  $J$  verschwindet dagegen nicht identisch, wenn wir die  $K_i$  als unabhängige Veränderliche betrachten.

Zufolge (21) ist  $\frac{p_i}{q_i}$  nicht konstant; sei z.B.

$$\frac{p_{m+1}}{q_{m+1}} \neq \frac{p_{m+2}}{q_{m+2}}, \quad \text{also} \quad \delta = p_{m+1} q_{m+2} - p_{m+2} q_{m+1} \neq 0.$$

Daher sind die Gleichungspaare

$$\left. \begin{aligned} p_{m+1} r_i + p_{m+2} s_i &= p_i \\ q_{m+1} r_i + q_{m+2} s_i &= q_i \end{aligned} \right\} \dots \dots \dots (22)$$

für  $i = 1, 2, \dots, m$  auflösbar. Die  $m$  Invarianten

$$K'_i = \frac{K_i}{K_{m+1}^{r_i} K_{m+2}^{s_i}} \quad (i = 1, 2, \dots, m)$$

sind dann absolute Invarianten und aus

$$\{K_1, K_2, \dots, K_{m+2}\} \equiv 0 \quad \{y\}$$

folgt (vgl. die letzten Gleichungen der ersten Mitteilung) dass auch

$$J' = \{K'_1, K'_2, \dots, K'_m, K_{m+1}, K_{m+2}\} \equiv 0 \quad \{y\}$$

ist.

Nun haben wir aber:

$$J' = (-1)^m \cdot \delta \cdot K_{m+1} \cdot K_{m+2} \cdot \frac{\partial (K'_1, K'_2, \dots, K'_m)}{\partial (t_1, t_2, \dots, t_m)};$$

also auch:

$$\frac{\partial (K'_1, K'_2, \dots, K'_m)}{\partial (t_1, t_2, \dots, t_m)} \equiv 0 \quad \{y\} \cdot \dots \cdot \dots \quad (23)$$

Weiters ist

$$\frac{\partial (K'_1, \dots, K'_m)}{\partial (t_1, \dots, t_m)} = \sum_{(x_1, \dots, x_m)} \frac{\partial (K'_1, \dots, K'_m)}{\partial (y_{x_1}, \dots, y_{x_m})} \cdot \frac{\partial (y_{x_1}, \dots, y_{x_m})}{\partial (t_1, \dots, t_m)},$$

also wegen (23), für jedes System  $a_1, a_2, \dots, a_m$ :

$$\frac{\partial (K'_1, \dots, K'_m)}{\partial (y_{a_1}, \dots, y_{a_m})} \equiv 0 \quad \{y\}.$$

Deshalb existiert wenigstens eine Beziehung

$$\Phi (K'_1, K'_2, \dots, K'_m) \equiv 0 \quad \{y\}$$

und daher auch wenigstens eine Identität der Gestalt

$$\Psi (K_1, K_2, \dots, K_{m+2}) \equiv 0 \quad \{y\} \cdot \dots \cdot \dots \quad (24)$$

zwischen allen  $m+2$  Invarianten  $K_i$ , wobei diese als Funktionen der  $y, y_\alpha, y_{\alpha\beta}, \dots$  betrachtet werden. (Als Funktionen der  $m$  Parameter  $t_i$  sind bereits  $m+1$  Invarianten stets untereinander abhängig).

Existiert umgekehrt eine Beziehung (24), die sich als Identität zwischen  $m$  absoluten Invarianten schreiben lässt, so kann man aus ihr auf

$$\{K_1, K_2, \dots, K_{m+2}\} \equiv 0 \quad \{y\}$$

schliessen.

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**Mathematics.** — "Ueber projektive Differentialinvarianten". IV. Von Prof. R. WEITZENBÖCK.

(Communicated at the meeting of February 28, 1925).

In dieser Mitteilung wird das Problem der Bestimmung aller projektiven Differentialinvarianten  $J$  einer  $m$ -dimensionalen Mannigfaltigkeit, die in einem linearen Raume von  $m+1$  Dimensionen liegt, auf eine Frage der Tensorrechnung zurückgeführt: Bestimmung der Invarianten einer Reihe "projektiver" Tensoren. Man erhält diese Reduktion auf eine ganz naturgemässe Weise, wenn man von den Eigenschaften  $G, P$  und  $H$  von  $J$  Gebrauch macht (Vgl. die erste Mitteilung).

Unsere Methode vereinigt die durch E. J. WILCZYNSKI <sup>1)</sup> bei  $m=2$  und allgemein durch G. FUBINI <sup>2)</sup> eingenommenen Standpunkte und kann unmittelbar bei den affinen Differentialinvarianten angewendet werden, wenn wir z.B.  $y_{m+2} \equiv 1$  setzen.

§ 1.

Eine projektive Differentialinvariante  $J$  hat, vgl. den Anfang der ersten Mitteilung, erstens die Eigenschaft  $G$  (Invarianz bei den linearen homogenen Transformationen

$$\zeta_i = a_{1i}x_1 + a_{2i}x_2 + \dots + a_{ni}x_n)$$

und ist daher eine Funktion von Klammerfaktoren  $(y_{\alpha_1} y_{\alpha_2} \dots y_{\alpha_{m+2}})$ .

Wir setzen wieder voraus dass

$$A = |(v' y_{ik})| = |(y y_1 \dots y_m y_{ik})| \neq 0 \quad \dots \quad (1)$$

ist. Dann sind nicht alle Klammerfaktoren  $(y y_1 \dots y_m y_{ik})$  Null und wir können z.B.  $(y y_1 \dots y_m y_{\alpha\beta}) \neq 0$  voraussetzen, wo  $\alpha$  und  $\beta$  fest gewählt sind.

Mit Hilfe der Identität ( $\nu =$  Ziffernkomples)

$$\left. \begin{aligned} (y y_1 \dots y_m y_{\alpha\beta}) y_\nu &= (y_\nu y_1 \dots y_m y_{\alpha\beta}) y + \\ &+ (y y_\nu y_2 \dots y_m y_{\alpha\beta}) y_1 + \dots + (y y_1 \dots y_m y_\nu) y_{\alpha\beta} \end{aligned} \right\} \quad (2)$$

ist dann jeder Klammerfaktor  $(y_{\nu_1} y_{\nu_2} \dots y_{\nu_{m+2}})$  ausdrückbar durch  $(y y_1 \dots y_m y_{\alpha\beta})$  und die Klammerfaktoren

$$(y_\nu y_1 \dots y_m y_{\alpha\beta}), (y y_1 \dots y_{i-1} y_\nu y_{i+1} \dots y_m y_{\alpha\beta}), (y y_1 \dots y_m y_\nu) \dots \quad (3)$$

<sup>1)</sup> E. J. WILCZYNSKI, Trans. Amer. Math. Soc. 8 (1907), p. 233; ibid. 9 (1908), p. 79; ibid. 10 (1909), p. 176.

<sup>2)</sup> G. FUBINI, Rend. di Palermo 43 (1918), p. 1. Ausführliche Litteratur in dem dieser Tage erscheinenden Artikel III D. 11 der „Enzyklopädie“ von L. BERWALD (Nr. 10 bis 12).

Wiederholte Anwendung dieses Resultates und der Gleichung

$$(y_{i_1} \dots y_{i_{m+1}} y_{i'}) = \frac{\partial (y_{i_1} \dots y_{i_{m+1}} y_{i'-1})}{\partial t_j} - (y_{i+1} y_{i_2} \dots y_{i'}) - \left. \begin{aligned} & - (y_{i_1} y_{i_2+1} y_{i_3} \dots y_{i'}) - \dots - (y_{i_1} \dots y_{i+i_{m+1}} y_{i'}) \end{aligned} \right\} \dots \quad (4)$$

gibt dann: jeder Klammerfaktor und deshalb auch jede Invariante ist ausdrückbar durch die Funktionen

$$\left. \begin{aligned} \varphi_1 &= (y y_1 \dots y_m y_{ik}) & \varphi_4 &= (y y_1 \dots y_m y_{ikt}) \\ \varphi_2 &= (y_{ik} y_1 \dots y_m y_{rs}) & \varphi_5 &= (y_{rs} y_1 \dots y_m y_{ikt}) \\ \varphi_3 &= (y_{ik} y_1 \dots y \dots y_m y_{rs}) & \varphi_6 &= (y_{rs} y_1 \dots y \dots y_m y_{ikt}) \end{aligned} \right\} \dots \quad (5)$$

und deren Ableitungen.

Hiebei ist in  $\varphi_3$  und in  $\varphi_6$  die Reihe  $y_h$  durch  $y$  ersetzt ( $h = 1, 2, \dots, m$ ).  $J$  ist zweitens invariant bei Parametertransformationen

$$t_i = t_i(\bar{t}_1, \dots, \bar{t}_m) \dots \dots \dots \quad (6)$$

und kann daher als Eliminationsresultat betrachtet werden, erhalten bei der Elimination der Ableitungen

$$\frac{\partial t_i}{\partial t_\lambda}, \frac{\partial^2 t_i}{\partial t_\lambda \partial t_\mu}, \dots$$

aus den Transformationsgleichungen der Funktionen (5) und ihrer Ableitungen. So haben wir z.B. bei  $\varphi_1$ :

$$\bar{y}_i = y_\lambda \cdot \frac{\partial t_\lambda}{\partial t_i} \quad , \quad \bar{y}_{ik} = y_{\lambda\mu} \frac{\partial t_\lambda}{\partial t_i} \frac{\partial t_\mu}{\partial t_k} + y_\lambda \frac{\partial^2 t_\lambda}{\partial t_i \partial t_k} :$$

$$(\bar{\varphi}_1)_{ik} = (\varphi_1)_{\lambda\mu} \cdot \frac{\partial t_\lambda}{\partial t_i} \cdot \frac{\partial t_\mu}{\partial t_k} \cdot \Delta.$$

Die Aufgabe: Elimination der  $\frac{\partial^2 t}{\partial t^2}$  aus den Transformationsgleichungen der Funktionen  $\varphi_i$  und ihrer Ableitungen wird nach FUBINI sehr vereinfacht, wenn wir die  $\varphi_i$  ersetzen durch Funktion  $\psi_i$ , die an Stelle der partiellen Ableitungen  $y_{ik}, y_{ikt}, \dots$  kovariante Ableitungen  $y_{i(k)}, y_{i(k)(l)}, \dots$  enthalten. Dies setzt die Kenntnis einer quadratischen Fundamentalform  $g_{ik} dt^i dt^k$  mit nicht-verschwindender Diskriminante  $g = |g_{ik}| \neq 0$  und vom  $\Delta$ -Gewichte Null voraus. Eine solche Form ist aber hier vorhanden:

$$f_2 = g_{ik} dt^i dt^k = \frac{F_2}{\sqrt{A}} \dots \dots \dots \quad (7)$$

Wir haben

$$\bar{f}_2 = f_2 \quad , \quad \tilde{f}_2 = \lambda^2 f_2 \quad \dots \dots \dots \quad (8)$$

d.h.  $f_2$  hat das  $\Delta$ -Gewicht Null und das  $\lambda$ -Gewicht 2.  $g_{ik}$  gibt also im

Parameterraum  $(t_1, t_2, \dots, t_m)$  einen kovarianten Tensor zweiter Stufe.

Mit Rücksicht auf die zweite der Gleichungen (8) sagen wir, dass  $g_{ik}$  ein "projektiver" Tensor mit  $\lambda$ -Gewicht 2 ist. Dagegen ist  $F_2$  eine "projektive Tensordichte" mit  $\Delta$ -Gewicht 1 und  $\lambda$ -Gewicht  $m + 2$ .

Tensoren des  $t$ -Raumes, die bei  $\tilde{y} = \lambda y$  invariant sind, nennen wir "projektive" Tensoren.

§ 2.

An Stelle von (5) nehmen wir nun die folgenden Funktionen:

$$\left. \begin{aligned} \psi_1 &= (y y_1 \dots y_m y_{i(k)}) \cdot A^{-\frac{1}{m+2}} = g_{ik} \\ \psi_2 &= (y_{i(k)} y_1 \dots y_m y_{r(s)}) \cdot A^{-\frac{1}{m+2}} = \varphi_{ik,rs} \\ \psi_3 &= (y_{i(k)} y_1 \dots y \dots y_m y_{r(s)}) \cdot A^{-\frac{1}{m+2}} = a_{ik,rs}^h \\ \psi_4 &= (y y_1 \dots y_m y_{i(k)(l)}) \cdot A^{-\frac{1}{m+2}} = h_{ik,l} \\ \psi_5 &= (y_{r(s)} y_1 \dots y_m y_{i(k)(l)}) \cdot A^{-\frac{1}{m+2}} = \vartheta_{rs,ik,l} \\ \psi_6 &= (y_{r(s)} y_1 \dots y \dots y_m y_{i(k)(l)}) \cdot A^{-\frac{1}{m+2}} = \eta_{rs,ik,l}^h \end{aligned} \right\} \dots (9)$$

Hiebei ist  $y_{i(k)}$  kovariante Ableitung des Vektors  $y_{(i)} = y_i = \frac{\partial y}{\partial t_i}$  bezüglich  $f_2$ , also:

$$y_{i(k)} = \frac{\partial y_i}{\partial t_k} - \Gamma_{ik}^\mu y_\mu = y_{ik} - \Gamma_{ik}^\mu y_\mu, \dots \dots \dots (10)$$

wo

$$\Gamma_{ik}^\mu = g^{\mu\nu} \Gamma_{\nu, ik} = \frac{1}{2} g^{\mu\nu} \left( \frac{\partial g_{\nu i}}{\partial t_k} + \frac{\partial g_{\nu k}}{\partial t_i} - \frac{\partial g_{ik}}{\partial t_\nu} \right)$$

die 3-Indicessymbole zweiter Art sind.

Weiters ist

$$y_{i(k)(l)} = \frac{\partial y_{i(k)}}{\partial t_l} - \Gamma_{il}^\mu y_{\mu(k)} - \Gamma_{kl}^\mu y_{i(\mu)} \dots \dots \dots (11)$$

$y_i$  ist ein kovarianter Vektor, aber wegen

$$\tilde{y} = \lambda y \quad \tilde{y}_i = \lambda \tilde{y}_i + \lambda_i y$$

kein projektiver Vektor. Ebenso sind  $y_{i(k)}$ ,  $y_{i(k)(l)}$  wohl Tensoren, aber keine projektiven Tensoren.

Mit Hilfe der Gleichungen (10) and (11) sind die  $\psi_i$  von (9) eindeutig durch die  $\varphi_i$  von (5) und umgekehrt aus zu drücken.

Unsere Aufgabe ist jetzt zurückgebracht auf die folgende: aus den

Transformationsgleichungen der Funktionen  $\psi_i$  und deren Ableitungen sind die Ableitungen  $\frac{\partial^2 t}{\partial t^s}$  zu eliminieren.

Wie verhalten sich nun die Funktionen  $\psi_i$  bei den Transformationen (6)? Wir haben

$$\bar{y} = y \cdot \bar{y}_i = y_\mu \frac{\partial t_\mu}{\partial \bar{t}_i} \quad , \quad (\bar{y}_1 \dots \bar{y}_m) = (y_1 \dots y_m) \cdot \Delta \quad , \quad \bar{A} = \Delta^{m+2} \cdot A$$

und finden deshalb:

$$\bar{g}_{ik} = g^{\lambda\mu} \frac{\partial t_\lambda}{\partial \bar{t}_i} \frac{\partial t_\mu}{\partial \bar{t}_k}$$

$$\bar{\varphi}_{ik,rs} = \varphi^{\lambda\mu,\rho\sigma} \frac{\partial t_\lambda}{\partial \bar{t}_i} \frac{\partial t_\mu}{\partial \bar{t}_k} \frac{\partial t_\rho}{\partial \bar{t}_r} \frac{\partial t_\sigma}{\partial \bar{t}_s}$$

und analog bei  $\psi_4$  und  $\psi_5$ . Bei  $\psi_3$  und  $\psi_6$  haben wir dagegen:

$$\bar{a}_{ik,rs}^h = a^{\nu,\mu,\rho\sigma} \frac{\partial t_\lambda}{\partial \bar{t}_i} \frac{\partial t_\mu}{\partial \bar{t}_k} \frac{\partial t_\rho}{\partial \bar{t}_r} \frac{\partial t_\sigma}{\partial \bar{t}_s} \cdot \frac{\partial \bar{t}_h}{\partial t_\nu}$$

$$\bar{\eta}_{rs,ik,t}^h = \eta^{\nu,\mu,\rho\sigma,\tau} \frac{\partial t_\rho}{\partial \bar{t}_r} \frac{\partial t_\sigma}{\partial \bar{t}_s} \frac{\partial t_\lambda}{\partial \bar{t}_i} \frac{\partial t_\mu}{\partial \bar{t}_k} \cdot \frac{\partial \bar{t}_h}{\partial t_\nu}$$

Die Funktionen  $\psi_i$  sind daher selbst Tensorkomponenten und unser Problem ist jetzt auf die viel einfachere Frage zurückgeführt: aus den Tensoren (9) und deren kovarianten Ableitungen sind Invarianten  $J$  aufzubauen, die auch bei den Transformationen  $\bar{y} = \lambda y$  die Invarianteneigenschaft besitzen.

§ 3.

Ein besonderer Fall der Identität (2) ist gegeben durch:

$$(yy_1 \dots y_m y_{i(k)}) y_{r(s)} = (y_{r(s)} y_1 \dots y_m y_{i(k)}) y - \Sigma (y_{r(s)} y_1 \dots y \dots y_m y_{i(k)}) y_h + \left. \begin{aligned} &+ (yy_1 \dots y_m y_{r(s)}) y_{r(k)} \end{aligned} \right\} \quad (12)$$

Teilen wir hier durch  $\sqrt[m+2]{\bar{A}}$ , dann haben wir nach (9):

$$g_{ik} y_{r(s)} = \varphi_{ik,rs} y + a_{ik,rs}^h y_h + g_{rs} y_{i(k)} \dots \dots \dots (13)$$

Hieraus folgt, wenn wir

$$Y = g^{rs} y_{r(s)} \dots \dots \dots (14)$$

und

$$a_{ik}^h = g^{rs} a_{ik,rs}^h = (y_{i(k)} y_1 \dots y \dots y_m Y) \cdot A^{-\frac{1}{m+2}} \dots \dots \dots (15)$$

$$\varphi_{ik} = g^{rs} \varphi_{ik,rs} = (y_{i(k)} y_1 \dots y_m Y) \cdot A^{-\frac{1}{m+2}} \dots \dots \dots (16)$$

setzen, wegen  $g^{ik} g_{ik} = m$ , die wichtige Beziehung <sup>1)</sup>:

$$m y_{i(k)} = \varphi_{ik} y - a_{ik}^h y_h + g_{ik} Y \dots \dots \dots (17)$$

<sup>1)</sup> G. FUBINI, l.c. § 5, (31).

Vermöge dieser Gleichung kann man die Tensoren (9) vereinfachen. Zunächst wird nämlich, wenn (17) in  $\psi_2$  von (9) einsetzen:

$$\varphi_{ik,rs} = \varphi_{ik} (yy_1 \dots y_m y_{(s)}) \cdot A^{-\frac{1}{m+2}} + g_{ik} (Yy_1 \dots y \dots y_m y_{(s)}) \cdot A^{-\frac{1}{m+2}},$$

also nach (16):

$$m \varphi_{ik,rs} = \varphi_{ik} g_{rs} - \varphi_{rs} g_{ik} \dots \dots \dots (18)$$

In (9) können wir also  $\varphi_{ik,rs}$  ersetzen durch  $\varphi_{ik}$ .

Bei  $\psi_3$  von (9) erhält man auf dieselbe Weise:

$$m a_{ik,rs}^h = a_{ik}^h g_{rs} - a_{rs}^h g_{ik} \dots \dots \dots (19)$$

Bei  $\psi_5$  haben wir:

$$m \vartheta_{rs,ik,l} = \varphi_{rs} h_{ik,l} + g_{rs} (Yy_1 \dots y_m y_{i(k)(l)}) \cdot A^{-\frac{1}{m+2}}$$

$$m \vartheta_{rs,ik,l} = \varphi_{rs} h_{ik,l} + g_{rs} \vartheta_{ik,l} \dots \dots \dots (20)$$

wobei

$$\vartheta_{ik,l} = (Yy_1 \dots y_m y_{i(k)(l)}) \cdot A^{-\frac{1}{m+2}} = g^{rs} \vartheta_{rs,ik,l} \dots \dots \dots (21)$$

gesetzt ist.

Schliesslich kommt bei  $\psi_6$ , wenn wir

$$\eta_{ik,l}^h = g^{rs} \eta_{rs,ik,l}^h = (Yy_1 \dots y \dots y_m y_{i(k)(l)}) \cdot A^{-\frac{1}{m+2}} \dots \dots \dots (22)$$

setzen:

$$m \eta_{rs,ik,l}^h = a_{rs}^h h_{ik,l} + g_{rs} \eta_{ik,l}^h \dots \dots \dots (23)$$

Also haben wir statt (9) die einfacheren Tensoren:

$$g_{ik} \cdot \varphi_{ik} \cdot a_{ik}^h \cdot h_{ik,l} \cdot \vartheta_{ik,l} \cdot \eta_{ik,l}^h \dots \dots \dots (24)$$

§ 4.

Jetzt wollen wir zeigen, dass wir den gemischten Tensor  $a_{ik}^h$  in (24) weglassen können.

Wir haben:

$$g_{ik} = (yy_1 \dots y_m y_{i(k)}) \cdot A^{-\frac{1}{m+2}}.$$

Differentieren wir dies kovariant, dann wird vermöge

$$g_{ik(l)} = \frac{\partial g_{ik}}{\partial t_l} - \Gamma_{il}^h g_{hk} - \Gamma_{ki}^h g_{ik} \equiv 0:$$

$$\left\{ \sum_h (yy_1 \dots y_{hl} \dots y_m y_{i(k)}) + (yy_1 \dots y_m y_{i(k)}) - \frac{1}{m+2} \frac{A_l}{A} (yy_1 \dots y_m y_{i(k)}) \right\} =$$

$$= [\Gamma_{k,il} + \Gamma_{i,kl}] \cdot A^{-\frac{1}{m+2}}$$

Setzen wir hier  $y_{hl}$  aus (10) und  $y_{i(k)l} = \frac{\partial y_{i(k)}}{\partial t_l}$  aus (11) ein, dann erhalten wir wegen (9):

$$(-\alpha_{hl,ik}^h + g_{ik} \Gamma_{hl}^h) + (h_{ik,l} + g_{hk} \Gamma_{il}^h + g_{ih} \Gamma_{kl}^h) - \frac{1}{m+2} \frac{A_l}{A} g_{ik} = \Gamma_{k,il} + \Gamma_{i,kl}$$

also wegen

$$\Gamma_{hl}^h = \frac{1}{2} \frac{\partial \log g}{\partial t_l} = \frac{1}{2} \frac{\partial \log A^{\frac{2}{m+2}}}{\partial t_l} = \frac{1}{m+2} \frac{A_l}{A} \quad \dots \quad (25)$$

$$\alpha_{hl,ik}^h = \alpha_{l,ik}^* = h_{ik,l} = (y y_1 \dots y_m y_{i(k)(l)}) \cdot A^{-\frac{1}{m+2}} \dots \quad (26)$$

Dabei entsteht der Tensor  $\alpha_{l,ik}^*$  aus  $\alpha_{cl,ik}^h$  durch Verjüngung.

Bei  $\alpha_{l,ik}^*$  und also auch bei  $h_{ik,l}$  können wir das Komma zwischen  $ik$  und  $l$  weglassen. Nach der Identität von RICCI<sup>1)</sup> ist nämlich

$$y_{i(k)(l)} - y_{i(l)(k)} = R_{i,kl}^h y_h \dots \quad (27)$$

wo  $R_{i,kl}^h$  der gemischte Krümmungstensor von  $g_{ik}$  ist. Nach (27) ist dann

$$(y y_1 \dots y_m y_{i(k)(l)}) = (y y_1 \dots y_m y_{i(l)(k)}),$$

also

$$h_{i,k,l} = h_{i,kl} = h_{kil} = h_{ilk} = \alpha_{ikl}^* \dots \quad (28)$$

ein symmetrischer Tensor dritter Stufe und das gleiche gilt nach (26) von  $\alpha_{l,ik}^*$ .

Der Tensor  $h_{ikl}$  ist nichts anderes als die kubische Differentialform

$$F_3 = (m+2) A [3 dF_2 - 2 (v' d^3 y)] - 3 F_2 \cdot dA.$$

Führen wir nämlich hier die kovarianten Ableitungen  $y_{i(k)}$  und  $y_{i(k)(l)}$  an Stelle von  $y_{ik}$  und  $y_{ikl}$  ein, so wird wegen

$$\frac{dA}{A} = \frac{m+2}{2} g^{ik} dg_{ik}$$

$$h_{ikl} dt^i dt^k dt^l = -\frac{1}{2(m+2)} F_3 \cdot A^{-\frac{1}{m+2}} \dots \quad (29)$$

Der Tensor  $\alpha_{ik,rs}^h$  ist nach (9) bezgl.  $ik$  und  $rs$  alternierend. Darum ist

$$\alpha_{ik,rs}^h = -\alpha_{rs,ik}^h = -\alpha_{sr,ik}^h = -h_{ikr} \dots \quad (30)$$

und

$$\alpha_{ik,rs}^v g^{ik} g^{rs} = \alpha_{ik}^v g^{ik} = 0 \dots \quad (31)$$

<sup>1)</sup> Vgl. z. B. mein Buch: Invariantentheorie, Groningen (1923), S. 345.

Setzen wir in (19)  $i = h$ , dann wird nach (26):

$$\begin{aligned} mh_{krs} &= a_{hk}^h g_{rs} - a_{rs}^h g_{hk} = a_k g_{rs} - a_{rs}^h g_{hk} \dots \dots \dots (32) \\ mh_{krs} g^{rs} &= ma_k - a_{rs}^h g_{rs} g_{hk} \end{aligned}$$

also

$$h_{krs} g^{rs} = a_k = a_{ik}^i \dots \dots \dots (33)$$

Multiplizieren wir dagegen (32) mit  $g^{ks}$ , dann ist nach (33):

$$\begin{aligned} mh_{krs} g^{ks} &= ma_r = a_k g_{rs} g^{ks} - a_{rs}^h g_{hk} g^{ks} = a_k \delta_r^k - a_{rs}^h \delta_h^s = 0, \\ a_l &= h_{ikl} g^{ik} = a_{il}^i = 0 \dots \dots \dots (34) \end{aligned}$$

Dies ist die bekannte Beziehung, die die Apolarität zwischen  $F_2$  und  $F_3$  ausdrückt.

(32) gibt dann wegen (34):

$$mh_{krs} = -a_{rs}^h g_{hk} ; \dots \dots \dots (35)$$

daher ist nach (26):

$$ma_{lik}^* = -a_{ik}^h g_{hl} \dots \dots \dots (36)$$

d.h. das Herunterholen von  $h$  in  $a_{ik}^h$  gibt bis auf den Faktor  $-m$  den Tensor  $a_{lik}^* = h_{lik}$ . Daher ist auch

$$a_{ik}^h = -mh_{ikl} g^{lh} = -mh_{ik}^h \dots \dots \dots (37)$$

und statt (17) kan man schreiben <sup>1)</sup>:

$$my_{i(k)} = \varphi_{ik} \cdot y + mh_{ikl} g^{lv} \cdot y_v + g_{ik} \cdot Y \dots \dots \dots (38)$$

Hiedurch ist nun der Tensor  $a_{ik,rs}^h$  und alle aus ihm mittels  $g_{\lambda\mu}$  und  $g^{\lambda\mu}$  hergeleiteten Tensoren reduziert auf  $h_{ikl}$  und wir können also in (9)  $\psi_3$ , also in (24)  $a_{ik}^h$  weglassen.

§ 5.

Statt (24) haben wir also noch die fünf Tensoren:

$$\left. \begin{aligned} g_{ik} &= (y y_1 \dots y_m y_{i(k)}) \cdot A^{-\frac{1}{m+2}} \\ \bar{g}_{ik} &= (y_{i(k)} y_1 \dots y_m Y) \cdot A^{-\frac{1}{m+2}} \\ h_{ikl} &= (y y_1 \dots y_m y_{i(k)(l)}) \cdot A^{-\frac{1}{m+2}} \\ \bar{h}_{ik,l} &= (Y y_1 \dots y_m y_{i(k)(l)}) \cdot A^{-\frac{1}{m+2}} \\ \eta_{ik,l}^h &= (Y y_1 \dots y \dots y_m y_{i(k)(l)}) \cdot A^{-\frac{1}{m+2}} \end{aligned} \right\} \dots \dots \dots (39)$$

<sup>1)</sup> G. FUBINI, Rend. Lincei V, 27 (1918), S. 147.

Wir untersuchen das Verhalten dieser Tensoren bei den Transformationen  $\tilde{y} = \lambda y$ . Wir haben

$$\tilde{y}_i = \lambda y_i + y \lambda_i$$

oder, wenn wir

$$\mu_i = \frac{\partial \log \lambda}{\partial t_i} = \frac{\lambda_i}{\lambda}$$

setzen:

$$\tilde{y}_i = \lambda (y_i + \mu_i y) \quad \dots \quad (40)$$

$g_{ik}$  ist bereits ein projektiver Tensor:

$$\tilde{g}_{ik} = \lambda^2 g_{ik} \quad , \quad \tilde{g}^{ik} = \frac{1}{\lambda^2} g^{ik}$$

Hieraus finden wir

$$\tilde{I}_{ik}^{\nu} = I_{ik}^{\nu} + \delta_i^{\nu} \mu_k + \delta_k^{\nu} \mu_i - g_{ik} \mu^{\nu} \quad (\mu^{\nu} = g^{\nu\alpha} \mu_{\alpha}) \quad \dots \quad (41)$$

Weiter aus (40):

$$\tilde{y}_{ik} = \lambda [y_{ik} + y_i \mu_k + y_k \mu_i + y (\mu_{ik} + \mu_i \mu_k)] \quad \left( \mu_{ik} = \frac{\partial \mu_i}{\partial t_k} \right) \quad \dots \quad (42)$$

$$\tilde{y}_{i(k)} = \frac{\partial \tilde{y}_i}{\partial t_k} - \tilde{I}_{ik}^{\nu} \tilde{y}_{\nu}$$

$$\tilde{y}_{i(k)} = \lambda [y_{i(k)} + g_{ik} \mu^{\rho} \mu_{\rho} + y (\mu_{ik} - I_{ik}^{\rho} \mu_{\rho} + g_{ik} \mu - \mu_i \mu_k)] \quad (\mu = \mu^{\rho} \mu_{\rho}) \quad (43)$$

$$\tilde{Y} = \tilde{g}^{ik} \tilde{y}_{i(k)} = \frac{1}{\lambda} [Y + m \mu^{\rho} y_{\rho} + y (g^{ik} \mu_{i(k)} + (m-1) \mu)] \quad \dots \quad (44)$$

Um aus diesen Transformationsgleichungen  $\mu_i$  und  $\mu_{ik}$  eliminieren zu können, benötigen wir eine Invariante  $M$  mit  $\Delta$ -Gewicht Null und  $\lambda$ -Gewicht eins<sup>1)</sup>. Ist nämlich

$$\bar{M} = M \quad , \quad \tilde{M} = \lambda^n \cdot M,$$

dann erhalten wir analog zu (43):

$$\begin{aligned} \tilde{M}_{i(k)} = \lambda^n \cdot [ & M_{i(k)} + g_{ik} M^{\rho} \mu_{\rho} + (n-1) (M_i \mu_k + M_k \mu_i) + \\ & + nM (\mu_{i(k)} + g_{ik} \mu + (n-2) \mu_i \mu_k) ] \end{aligned}$$

also bei  $n=1$ :

$$\tilde{M}_{i(k)} = \lambda [M_{i(k)} + g_{ik} M^{\rho} \mu_{\rho} + M (\mu_{i(k)} + g_{ik} \mu - \mu_i \mu_k)] \quad \dots \quad (45)$$

Nach (43) und (45) wird somit:

$$\tilde{M} \tilde{y}_{i(k)} - \tilde{y} \tilde{M}_{i(k)} = \lambda^2 [M y_{i(k)} - y M_{i(k)} + M g_{ik} \mu^{\rho} y_{\rho} - y g_{ik} M^{\rho} y_{\rho}]$$

Wegen

<sup>1)</sup> Es ist dabei gleichgültig, wie diese Invariant  $M$  entsteht.

$$\mu_{\rho} = \frac{\bar{M}_{\rho}}{\bar{M}} - \frac{M_{\rho}}{M} \quad , \quad \bar{M} \bar{y}_{\rho} - \bar{y} \bar{M}_{\rho} = \lambda^2 (M y_{\rho} - y M_{\rho})$$

folgt daher, dass

$$M y_{i(k)} - g_{ik} M^{\rho} y_{\rho} + y \left( g_{ik} \frac{M^{\rho} M_{\rho}}{M} - M_{i(k)} \right) \quad . \quad . \quad (46)$$

ein projektiver Tensor mit  $\lambda$ -Gewicht 2 ist.

Hieraus finden wir die absolute projektive Invariante

$$Z = MY - mM^{\rho} y_{\rho} + y \left( m \frac{M^{\rho} M_{\rho}}{M} - g^{ik} M_{i(k)} \right) \quad . \quad . \quad . \quad (47)$$

Auch der Tensor  $h_{i(k)}$  ist bereits projektiv und hat das  $\lambda$ -Gewicht 2:

$$\tilde{h}_{i(k)} = \lambda^2 h_{i(k)}$$

Bei  $\varphi_{ik}$  haben wir nach (39), (43), (44) und

$$(v'Y) = (y y_1 \dots y_m Y) = m \cdot A^{\frac{1}{m+2}} \quad . \quad . \quad . \quad (48)$$

$$(y_{i(k)} y_1 \dots y \dots y_m Y) = a_{ik}^h \cdot A^{\frac{1}{m+2}} \quad . \quad . \quad . \quad (49)$$

$$\varphi_{ik} = \varphi_{ik} - g_{ik} (g^{rs} \mu_{r(s)} + (m-1) \mu) + m (\mu_{i(k)} + g_{ik} \mu - \mu_i \mu_k) + a_{ik}^h \mu_h \quad (50)$$

Hier können wir nun nach (45) und

$$\tilde{g}^{rs} \bar{M}_{r(s)} = \frac{1}{\lambda} [g^{rs} M_{r(s)} + mM^{\rho} \mu_{\rho} + M (g^{rs} \mu_{r(s)} + (m-1) \mu)] \quad . \quad (51)$$

die Ausdrücke zwischen den Klammern eliminieren ( $g^{rs} M_{r(s)}$  ist der "zweite Differentialparameter"  $\Delta_2 M$  von  $M$ ). Wir erhalten so den projektiven Tensor

$$f_{ik} = M \varphi_{ik} - mM_{i(k)} + g_{ik} g^{rs} M_{r(s)} - a_{ik}^v M_v \quad . \quad . \quad . \quad (52)$$

$$\tilde{f}_{ik} = \lambda \cdot f_{ik} \quad . \quad . \quad . \quad (53)$$

Dieser projektive Tensor kommt also an die Stelle des (nicht-projektiven) Tensors  $\varphi_{ik}$ . Wie man aus (52) ablesen kann, ist

$$f_{ik} g^{ik} = 0 \quad . \quad . \quad . \quad (54)$$

Die zweite quadratische Differentialform  $f_{ik} dt^i dt^k$  ist also mit  $g_{ik}$  apolar. Benützen wir (37), dann haben wir statt (52) auch:

$$f_{ik} = M \varphi_{ik} - mM_{i(k)} + g_{ik} g^{rs} M_{r(s)} + m h_{i(k)} M^i \quad . \quad . \quad (55)$$

Ist  $M=1$ , so wird  $f_{ik} = \varphi_{ik}$  und nach (47)  $Z=Y$ . Setzt man  $\bar{M}=1$  in  $\bar{M} = \lambda M$ , also

$$\lambda = \frac{1}{M} \quad . \quad . \quad . \quad (56)$$

dann sind  $\bar{y} = \lambda y = \frac{y}{M}$  Normalkoordinaten, analog mit den projektiven Normalkoordinaten von FUBINI.

Die grundlegende Gleichung (38) kann nach (55) wie folgt geschrieben werden :

$$mMy_{i(k)} = y(f_{ik} + mM_{i(k)} - g_{ik}g^{rs}M_{r(s)} - mh_{ikl}M^l) + mMh_{ikl}g^l y_v + Mg_{ik}Y \quad (57)$$

Drücken wir hier noch  $MY$  nach (47) durch  $Z$  aus, so bekommen wir :

$$mMy_{i(k)} = y \left( f_{ik} + mM_{i(k)} - mg_{ik} \frac{M^r M_p}{M} - mh_{ikl}M^l \right) + \left. \begin{aligned} & + m(Mh_{ik}^v + M^v g_{ik}) y_v + g_{ik} Z. \end{aligned} \right\} \quad (58)$$

§ 6.

Statt (58) schreiben wir kürzer

$$mMy_{i(k)} = yp_{ik} + q_{ik}^v y_v + g_{ik} Z, \quad \dots \quad (59)$$

setzen also :

$$p_{ik} = f_{ik} + mM_{i(k)} - mg_{ik} \frac{M^r M_p}{M} - mh_{ikl}M^l \quad \dots \quad (60)$$

$$q_{ik}^v = m(Mh_{ik}^v + g_{ik}M^v) \quad \dots \quad (61)$$

Differenzieren wir (38) kovariant nach  $t_l$  so wird :

$$my_{i(k)(l)} = y \varphi_{ik(l)} + y_l \varphi_{ik} + mh_{ik(l)}^v y_v + mh_{ik}^v y_{h(l)} + g_{ik} Y_l \quad \dots \quad (62)$$

Setzen wir dies nun in  $\vartheta_{ik,l}$  und  $\eta_{ik,l}^v$  (vgl. (39)) ein, dann sehen wir, dass sich diese Tensoren durch  $g_{ik}$ ,  $\varphi_{ik}$ ,  $h_{ikl}$  und die zwei folgenden

$$(y_{i(k)} y_1 \dots y_m Y_l) \cdot A^{-\frac{1}{m+2}} \quad , \quad (y_{i(k)} y_1 \dots y \dots y_m Y_l) \cdot A^{-\frac{1}{m+2}}$$

ausdrücken lassen. In diesen beiden können wir nach (47)  $Z$  statt  $Y$  einführen und bekommen als neue Tensoren die folgenden :

$$q_{ik,l} = (y_{i(k)} y_1 \dots y_m Z_l) \cdot A^{-\frac{1}{m+2}} \quad , \quad \varepsilon_{ik,l}^v = (y_{i(k)} y_1 \dots y \dots y_m Z_l) \cdot A^{-\frac{1}{m+2}}. \quad (63)$$

Statt (24) haben wir jetzt

$$g_{ik} \quad , \quad f_{ik} \quad , \quad h_{ikl} \quad , \quad q_{ik,l} \quad , \quad \varepsilon_{ik,l}^v \quad , \quad \dots \quad (64)$$

Nach (48) und (47) finden wir

$$(v'Z) = (y y_1 \dots y_m Z) = mM \cdot A^{-\frac{1}{m+2}} \quad \dots \quad (65)$$

Hieraus folgt nach (47), (10), (25) und (34) :

$$(v'Z_l) = 0 \quad \dots \quad (66)$$

Berechnen wir nun  $\tilde{\varepsilon}_{ik,l}^v$ , dann bekommen wir nach (66) und wegen  $\tilde{Z} = Z, \tilde{Z}_i = Z_i$  :

$$\tilde{\varepsilon}_{ik,l}^{\nu} = \lambda \cdot \varepsilon_{ik,l}^{\nu} \dots \dots \dots (67)$$

d.h.  $\tilde{\varepsilon}_{ik,l}^{\nu}$  ist bereits ein projektiver Tensor.

Bei  $\varrho_{ik,l}$  dagegen haben wir

$$\tilde{\varrho}_{ik,l} = \lambda \varrho_{ik,l} + \varepsilon_{ik,l}^{\nu} \mu_{\nu}$$

Ist nun wieder  $N$  eine projektive Differentialinvariante mit  $\Delta$ -Gewicht Null und  $\lambda$ -Gewicht 1, dann haben wir, so wie oben bei der Invariante  $M$  (man könnte auch  $M = N$  nehmen):

$$\mu_{\nu} = \frac{\tilde{N}_{\nu}}{\tilde{N}} - \frac{N_{\nu}}{N}$$

Also ist nicht  $\varrho_{ik,l}$  selbst, sondern

$$\sigma_{ik,l} = \varrho_{ik,l} - \varepsilon_{ik,l}^{\nu} \frac{N_{\nu}}{N} \dots \dots \dots (68)$$

ein projektiver Tensor.

Nun können wir  $\sigma_{ik,l}$  und  $\varepsilon_{ik,l}^h$  mit Hilfe von (38) noch vereinfachen.

Drücken wir  $y_{(k)}$  in  $(y_{(k)} y_1 \dots y_m Z_l)$  nach (38) aus, dann haben wir nach (63) und (66):

$$\begin{aligned} \varepsilon_{ik,l}^{\nu} &= \frac{1}{m} g_{ik} (Y y_1 \dots y \dots y_m Z_l) \cdot A^{-\frac{1}{m+2}} \\ \varepsilon_{ik,l}^{\nu} &= \frac{1}{m} g_{ik} g^{rs} \varepsilon_{rs,l}^{\nu} = \frac{1}{m} g_{ik} \varepsilon_l^{\nu} \dots \dots \dots (69) \end{aligned}$$

Statt  $\varepsilon_{ik,l}^{\nu}$  haben wir also jetzt den projektiven Tensor

$$\varepsilon_l^{\nu} = (Y y_1 \dots y \dots y_m Z_l) \cdot A^{-\frac{1}{m+2}} \dots \dots \dots (70)$$

Bei  $\varrho_{ik,l}$  finden wir auf dieselbe Art:

$$\begin{aligned} \varrho_{ik,l} &= \frac{1}{m} g_{ik} (Y y_1 \dots y_m Z_l) \cdot A^{-\frac{1}{m+2}} \\ &= \frac{1}{m} g_{ik} g^{rs} \varrho_{rs,l} = \frac{1}{m} g_{ik} \varrho_l \end{aligned}$$

Also kommt statt (68):

$$\sigma_l = \varrho_l - \varepsilon_l^{\nu} \frac{N_{\nu}}{N} \dots \dots \dots (71)$$

wo

$$\sigma_l = (Y y_1 \dots y_m Z_l) \cdot A^{-\frac{1}{m+2}} \dots \dots \dots (72)$$

Daher haben wir schliesslich statt (64) die projektiven Tensoren:

$$g_{ik} \ , \ f_{ik} \ , \ h_{ikl} \ , \ \sigma_l \ , \ \varepsilon_l^{\nu} \dots \dots \dots (73)$$

Hierbei sind die Tensoren  $f_{ik}$  und  $\varepsilon_l^{\nu}$  mit Hilfe der Invariante  $M$ , dagegen der Tensor  $\sigma_l$  mit Hilfe der Invarianten  $M$  und  $N$  hergeleitet. Die Reduktion der beiden letzten Tensoren  $\sigma_l$  und  $\varepsilon_l^{\nu}$  soll den Gegenstand einer folgenden Mitteilung bilden.

**Chemistry.** — “Equilibria in systems, in which phases, separated by a semipermeable membrane. VI. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of February 28, 1925).

In the previous communications we have discussed some simple cases of osmose in binary and ternary systems. We now shall deduce some general properties.

*The osmotic water-attraction of a system of phases.*

In our previous considerations we have discussed already the O.W.A. of a liquid and in some simple cases also that of one or more solid substances; now we shall consider more general cases. We take the osmotic equilibrium:

$$E = [E_1(n_1 r_1) | E_2(n_2 r_2) \dots \dots \dots] \quad (1)$$

in which  $E_1$  is a system of  $n_1$  components in  $r_1$  phases under the pressure  $P_1$  and  $E_2$  a system of  $n_2$  components in  $r_2$  phases under the pressure  $P_2$ .

We now imagine that a small quantity of water (in general: of the diffusing substance) passes from the system  $E_2$  into the system  $E_1$ ; then the thermodynamical potential of the system  $E_1$  will change with  $\delta Z_1$ , that of the system  $E_2$  with  $\delta Z_2$ . When  $\delta Z_1 + \delta Z_2 \geq 0$ , then system (1) is in equilibrium, when  $\delta Z_1 + \delta Z_2 < 0$ , then water will diffuse through the membrane. In order to define the direction, in which the water will diffuse through the membrane, we have to know  $\delta Z_1$  and  $\delta Z_2$ . Firstly we shall define  $\delta Z_1$  for the system  $E_1$ ; for this we distinguish different cases.

*I. The system  $E_1$  consists of a liquid only.*

We call the  $n_1$  components, of which the liquid  $L_1$  consists,  $XY\dots W$ ; we represent the composition of the liquid by:

$$x_1 \text{ Mol } X + y_1 \text{ Mol } Y \dots + (1 - x_1 - y_1 \dots) \text{ Mol } W.$$

We assume that there are  $q_1$  quantities of this liquid  $L_1$ , each with the thermodynamical potential  $\zeta_1$ . When a small quantity  $\mu$  of the diffusing substance  $W$  passes from the system  $E_2$  into those  $q_1$  quantities of the liquid  $L_1$ , then follows:

$$\delta Z_1 = (q_1 + \mu) \left( \zeta_1 + \frac{\partial \zeta_1}{\partial x_1} dx_1 + \frac{\partial \zeta_1}{\partial y_1} dy_1 \dots \right) - q_1 \zeta_1.$$

As, when  $\mu$  is infinitely small with respect to  $q_1$ ,

$$dx_1 = \frac{q_1 x_1}{q_1 + \mu} - x_1 = -\frac{\mu}{q_1} x_1 \quad dy_1 = \frac{q_1 y_1}{q_1 + \mu} - y_1 = -\frac{\mu}{q_1} y_1$$

etc. we may write also:

$$\delta Z_1 = \left( \zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} - \dots \right) \mu = \varphi_1 \mu \dots \dots (2)$$

Previously we have seen that the value of  $\varphi_1$  in connection with a corresponding value of the system  $E_2$  decides whether the substance  $W$  will diffuse from the liquid  $L_1$  towards the system  $E_2$  or reversally; for the sake of abbreviation we shall say therefore that  $\varphi_1$  defines the O.W.A. of the liquid  $L_1$ .

II. *The system  $E_1$  consists of two or more liquids.*

When two or more liquids are in equilibrium with one another, then they are isotonic with respect to all components; consequently they also have the same O.W.A. It is obvious, therefore, also that the O.W.A. of a complex of liquids is equal to the O.W.A. of each of them, separately. We are able to prove this still also in the following way. For the sake of simplicity we take a system of two liquids viz.

$$E_1 = L_1 + L_2 \dots \dots \dots (3)$$

We represent the composition of

$$L_1 \text{ by } x_1 \text{ Mol } X + y_1 \text{ Mol } Y \dots + (1 - x_1 - y_1 \dots) \text{ Mol } W$$

$$L_2 \text{ by } x_2 \text{ Mol } X + y_2 \text{ Mol } Y \dots + (1 - x_2 - y_2 \dots) \text{ Mol } W.$$

We take  $q_1$  quantities of  $L_1$  and  $q_2$  quantities of  $L_2$ , each with the thermodynamical potential  $\zeta_1$  and  $\zeta_2$ . We now imagine that a small quantity  $\mu$  of the diffusing substance  $W$  passes from the system  $E_2$  into the system  $E_1$ . When  $a_1$  quantities of  $W$  go towards the  $q_1$  quantities of  $L_1$  and  $a_2$  quantities of  $W$  towards the  $q_2$  quantities of  $L_2$ , then is, therefore  $a_1 + a_2 = \mu$ . Further we assume that at the same time  $\delta n_x \delta n_y \dots \delta n_w$  quantities of the substances  $XY \dots W$  pass from the  $q_2$  quantities of  $L_2$  into the  $q_1$  quantities of  $L_1$ . We now have:

$$\delta Z_1 = (q_1 + \Delta + a_1) \left( \zeta + \frac{\partial \zeta}{\partial x} dx + \frac{\partial \zeta}{\partial y} dy \dots \right)_1 \dots \dots (4)$$

$$+ (q_2 - \Delta + a_2) \left( \zeta + \frac{\partial \zeta}{\partial x} dx + \frac{\partial \zeta}{\partial y} dy \dots \right)_2 - q_1 \zeta_1 - q_2 \zeta_2$$

in which  $\Delta = \delta n_x + \delta n_y \dots + \delta n_w$ .

Further we find:

$$q_1 dx_1 = \delta n_x - x_1 (\Delta + a_1) \quad q_2 dx_2 = -\delta n_x + x_2 (\Delta - a_2)$$

$$q_1 dy_1 = \delta n_y - y_1 (\Delta + a_1) \quad q_2 dy_2 = -\delta n_y + y_2 (\Delta - a_2)$$

etc. With the aid of this (3) passes into:

$$\delta Z_1 = (\varphi_1 - \varphi_2) \Delta + \left( \frac{\partial \zeta_1}{\partial x_1} - \frac{\partial \zeta_2}{\partial x_2} \right) \delta n_x + \left( \frac{\partial \zeta_1}{\partial y_1} - \frac{\partial \zeta_2}{\partial y_2} \right) \delta n_y + \varphi_1 a_1 + \varphi_2 a_2 \quad (5)$$

in which:

$$\begin{aligned} \varphi_1 &= \zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} \dots \\ \varphi_2 &= \zeta_2 - x_2 \frac{\partial \zeta_2}{\partial x_2} - y_2 \frac{\partial \zeta_2}{\partial y_2} \dots \end{aligned}$$

We now imagine firstly the system (3) by itself so that  $a_1 = 0$  and  $a_2 = 0$ . Then follow from (5) the known equations for equilibrium:

$$\varphi_1 = \varphi_2 \quad \frac{\partial \zeta_1}{\partial x_1} = \frac{\partial \zeta_2}{\partial x_2} \quad \frac{\partial \zeta_1}{\partial y_1} = \frac{\partial \zeta_2}{\partial y_2} \text{ etc. } \dots \dots \quad (6)$$

When now, as is assumed above,  $\mu = a_1 + a_2$  quantities of  $W$  diffuse from  $E_2$  towards the two liquids and when we assume that both these liquids are in equilibrium with one another, then (5) passes, therefore, into:

$$\delta Z_1 = \varphi_1 a_1 + \varphi_2 a_2 = \varphi_1 \mu = \varphi_2 \mu. \dots \dots \quad (7)$$

Consequently it is apparent from this, as is already said above, that the O.W.A. of liquid  $L_1$  is equal to that of  $L_2$  and equal to that of the complex  $L_1 + L_2$ .

III. *The system  $E_1$  contains, besides one or more liquids, still other phases.*

In the examples, discussed already formerly, we have seen that the O.W.A. of a binary or ternary liquid, which is saturated with a solid substance, is equal to the O.W.A. of the liquid only. Consequently the O.W.A. of a liquid does not change by the presence of a solid substance, with which it is in equilibrium. Generally this is the case. Let us take f. i. the system:

$$E_1 = L_1 + L_2 \dots + F_1 + F_2 + \dots$$

in which  $L_1, L_2$  etc. represent liquids and  $F_1, F_2 \dots$  other phases. Then the O.W.A. of  $L_1$  is equal to that of  $L_2$  etc. and equal to that of the total system  $E_1$ .

In order to show this for a system

$$E_1 = L + F_1 + F_2 \dots + F_{r-1} \dots \dots \quad (8)$$

we represent the composition of

$$\begin{aligned} L &\text{ by } x \text{ Mol } X + y \text{ Mol } Y \dots + (1 - x - y \dots) \text{ Mol } W \\ F_1 &\text{ ,, } a_1 \text{ Mol } X + \beta_1 \text{ Mol } Y \dots + (1 - a_1 - \beta_1 \dots) \text{ Mol } W \\ F_2 &\text{ ,, } a_2 \text{ Mol } X + \beta_2 \text{ Mol } Y \dots + (1 - a_2 - \beta_2 \dots) \text{ Mol } W \end{aligned}$$

etc.; we call the thermodynamical potentials  $\zeta, \zeta_1, \zeta_2$  etc.

We now imagine that a small quantity  $\mu$  of the diffusing substance

$W$  passes from a system  $E_2$  into the system  $E_1$ ; this will cause also that  $\delta n_1 \delta n_2 \dots$  quantities of the phases  $F_1 F_2 \dots$  pass into the liquid  $L$ . The change of the thermodynamical potential of the system  $E$  then is:

$$\delta Z_1 = (q + \Delta + \mu) \left( \zeta + \frac{\partial \zeta}{\partial x} dx + \frac{\partial \zeta}{\partial y} dy \dots \right) - q\zeta - \zeta_1 \delta n_1 - \zeta_2 \delta n_2 \dots \quad (9)$$

in which:  $\Delta = \delta n_1 + \delta n_2 \dots + \delta n_{r-1}$ . Further is assumed that in the equilibrium (8)  $q$  quantities of liquid occur. When we represent the quantities of the components  $X Y \dots W$ , which pass into the liquid, by  $\delta n_x \delta n_y \dots \delta n_w$ , then they are defined by:

$$\begin{aligned} \delta n_x &= a_1 \delta n_1 + a_2 \delta n_2 + a_3 \delta n_3 \dots \\ \delta n_y &= \beta_1 \delta n_1 + \beta_2 \delta n_2 + \beta_3 \delta n_3 \dots \end{aligned} \quad (10)$$

etc. Hence follows the relation:

$$\delta n_x + \delta n_y \dots + \delta n_w = \Delta + \mu.$$

Now we find for the values, which we have to give to  $dx dy \dots$  in (9):

$$q \cdot dx = \delta n_x - x(\Delta + \mu)$$

$$q \cdot dy = \delta n_y - y(\Delta + \mu)$$

etc. With the aid of this (9) passes into:

$$\delta Z_1 = \left( \zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \dots \right) (\Delta + \mu) - \zeta_1 \delta n_1 - \zeta_2 \delta n_2 \dots + \frac{\partial \zeta}{\partial x} \cdot \delta n_x + \frac{\partial \zeta}{\partial y} \cdot \delta n_y \dots \quad (11)$$

If we imagine in (11) the values of  $\delta n_x \delta n_y \dots$  from (10), to be substituted then it appears that (11) contains besides  $\mu$  still the  $r-1$  variations  $\delta n_1 \delta n_2 \dots$ .

Firstly we take the system (8) by itself, so that  $\mu = 0$ . Then follow from (11) the known  $r-1$  equations for equilibrium

$$\zeta - \zeta_i + (a_i - x) \frac{\partial \zeta}{\partial x} + (\beta_i - y) \frac{\partial \zeta}{\partial y} + \dots = 0 \quad (12)$$

$$i = 1, 2, \dots (r-1)$$

When, as is assumed above,  $\mu$  quantities of the substance  $W$  diffuse towards the system  $E_1$  and when we assume that this system is in equilibrium, then (11) passes into:

$$\delta Z_1 = \left( \zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \dots \right) \mu \quad (13)$$

The O.W.A. of the whole system (8) is the same, therefore, as that of the liquid.

Of course the considerations above are also true, when one of the solid phases is the diffusing substance  $W$ .

IV. *The system  $E_1$  consists of solid substances only.*

We take a system:

$$E_1(n, r) = F_1 + F_2 \dots + F_r \dots \dots \dots (14)$$

of  $n$  components in  $r$  phases, we represent the composition of a phase  $F_i$  by:

$$u_i \text{ Mol } X + \beta_i \text{ Mol } Y \dots + (1 - u_i - \beta_i \dots) \text{ Mol } W$$

$$i = 1, 2, \dots, r$$

We assume that those solid phases have a constant composition. We now may distinguish several cases, according to the fact whether from system (14) by acceptance or loss of a small quantity of the diffusing substance  $W$  a liquid arises or not.

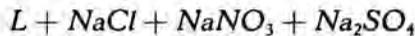
1°. *A liquid arises.*

When we take a system as f. i.



of course this cannot lose water but it can take in water.

In the latter case it passes into:



in which  $L$  is a liquid saturated with the solid substances. However, there are also systems which can form a liquid, also with loss of water.

A simple example is a. o. the hydrate  $Fe_2Cl_6 \cdot 12H_2O$  f. i. at  $30^\circ$ ; this passes, when we withdraw from it a little water, into the equilibrium  $L + Fe_2Cl_6 \cdot 12H_2O$ , in which the liquid  $L$  contains more  $Fe_2Cl_6$  than the hydrate. Consequently we distinguish two cases.

a. *The liquid is formed, when the system takes the diffusing substance.*

In the previous communication we have put in some simple cases of ternary systems the O.W.A. of one or two solid substances equal to that of the liquid, which arises at the acceptance of a small quantity of water. That this is generally the case, appears a. o. in the following way. We assume that system (14) by acceptance of a small quantity of the diffusing substance  $W$  passes into the system:

$$L + F_1 + F_2 \dots + F_r \dots \dots \dots (15)$$

We give to  $L$  the composition:

$$x \text{ Mol } X + y \text{ Mol } Y \dots + (1 - x - y \dots) \text{ Mol } W.$$

When this liquid arises by the liquefaction of  $\delta n_1$  quantities of  $F_1 + \delta n_2$  quantities of  $F_2$  etc., with  $\mu$  quantities of  $W$ , then we have:

$$x = \frac{a_1 \delta n_1 + a_2 \delta n_2 \dots}{\Delta + \mu} ; y = \frac{\beta_1 \delta n_1 + \beta_2 \delta n_2 \dots}{\Delta + \mu} ; \dots (16)$$

etc. in which

$$\Delta = \delta n_1 + \delta n_2 \dots + \delta n_r .$$

The change of the thermodynamical potential then is:

$$\delta Z_1 = \zeta (\Delta + \mu) - \zeta_1 \delta n_1 - \zeta_2 \delta n_2 \dots (17)$$

When we assume that system (15) is in equilibrium, then  $r$  equations of the form (12) are valid for this. With the aid of those and of (16) we find:

$$\zeta \cdot \Delta + \left( x \frac{\partial \zeta}{\partial x} + y \frac{\partial \zeta}{\partial y} + \dots \right) \mu - \zeta_1 \delta n_1 - \zeta_2 \delta n_2 \dots = 0$$

so that (17) passes into:

$$\delta Z_1 = \left( \zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} - \dots \right) \mu \dots (18)$$

Hence follows that the O.W.A. of a system of solid phases is equal to the O.W.A. of the liquid, which arises when the system takes a little of the diffusing substance.

*b. The liquid is formed, when the system loses the diffusing substance.*

We now find the same as in case a. By recapitulation of both cases, it follows:

when in a system of solid substances a liquid  $L_1$  is formed with acceptance of the diffusing substance  $W$  and a liquid  $L_2$  is formed with loss of this substance  $W$ , then the O.W.A. of this system has two values; the one is equal to that of liquid  $L_1$  and is valid for the acceptance, the other to that of liquid  $L_2$  and is valid for the loss of the diffusing substance.

In the previous communications we have discussed already some simple examples.

2. *Two or more liquids arise,*

After the former considerations it is not necessary to discuss this case more in detail.

3. *No liquid arises.*

When a system  $E_1$  of solid substances takes a little of the diffusing substance  $W$  f.i. water and no liquid is formed, then this taken water must be held in any way by the solid substances, or it must be deposited like ice or it must occur as watervapour. Let us take f.i. the system:



which consists of one substance only; this may pass by acceptance of water into the system:



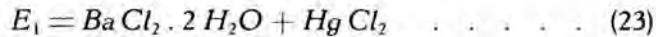
The system



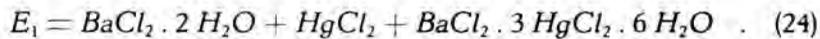
may pass into:



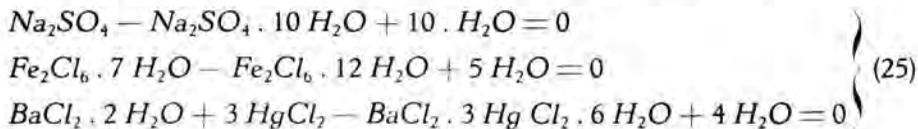
and the system:



below  $17^{\circ}.2$  into the system:



We represent the reactions occurring in those systems by

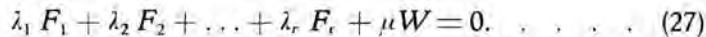


From the systems 19, 21 and 23 a new phase arises, therefore, by acceptance of water; this is no more the case in the systems 20, 22 and 24 which have originated from those; only the quantities of the phases, which are present already, change in them. The same is true also, when we withdraw a little water from those systems 20, 22 and 24. Consequently we may say that in those systems at acceptance or loss of water a phases-reaction occurs, as is represented in (25), viz. a reaction, at which not the composition but only the quantity of the phases changes. As the systems 19, 21 and 23 by acceptance of a very small quantity of water pass at once already into 20, 22 and 24, we shall consider the latter only, consequently systems, in which at acceptance or loss of the diffusing substance a phases-reaction occurs.

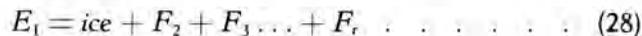
We now take a similar system:



we represent the reaction, when  $\mu$  quantities of the diffusing substance  $W$  are taken in by:



In this [compare the reactions 25] some of the reaction-coefficients are positive, and other ones negative. Of course it may be also the case that one or more of the phases of (26) do not participate in the reaction<sup>1)</sup>, the corresponding reaction-coefficients in 27 are zero then. A simple case we have f.i. in the system:



<sup>1)</sup> Then we have a singular equilibrium. Compare for this: F. A. H. SCHREINEMAKERS: In-, mono- and plurivariants equilibria. XXVII and XXVIII.

when water is the diffusing substance. Reaction (27) then becomes:

$$-\mu \text{ quantities of ice} + \mu \text{ quantities of water} = 0. \quad \dots \quad (29)$$

or in the ordinary form: water  $\rightleftharpoons$  ice.

When system 26 takes in  $\mu$  quantities of the diffusing substance  $W$ , then is the change of the thermodynamical potential:

$$\delta Z_1 = -\lambda_1 \zeta_1 - \lambda_2 \zeta_2 \dots - \lambda_r \zeta_r. \quad \dots \quad (30)$$

As viz. the quantity of a phase decreases when this is negative [compare f. i. the reactions 25], we must give in 30 the negative sign to  $\lambda_1 \lambda_2 \dots$

We now take a liquid  $L$  which is in equilibrium with the system 26. This is always possible. Let us take f. i. the system  $Na_2SO_4 + Na_2SO_4 \cdot 10H_2O$  at a definite temperature  $T_1$  and under a definite pressure  $P_1$  and let us consider the system:



at the same  $T_1$  and  $P_1$ . Then we have three phases, while  $T_1$  and  $P_1$  are given; consequently the liquid must contain three components at least. When it contains three components, then its composition is completely defined; when it contains four components, then it is represented by the points of a curve in space; etc.

When we take the system with the two ternary double-salts.  $D . a H_2O + D . \beta . H_2O$ , so that in this a phases-reaction may occur by acceptance or loss of water. Then the liquid of the equilibrium  $D . a H_2O + D . \beta H_2O + L$  must contain also three components at least. As the solid phases are ternary compounds, the liquid, however, contains already from itself the three components. Consequently we need not add one or more new components, as in the previous system. The composition of the ternary liquid  $L$  is completely defined; in general there are two different ternary liquids, which may be in equilibrium with  $D . a H_2O + D . \beta H_2O$ .

We now consider the equilibrium;

$$F_1 + F_2 + F_3 \dots + F_r + L \quad \dots \quad (31)$$

The compositions of the solid phases are represented by:

$$a_i \text{ Mol } X + \beta_i \text{ Mol } Y \dots + (1 - a_i - \beta_i \dots) \text{ Mol } W$$

$$i = 1, 2 \dots r$$

that of the liquid  $L$ , which contains, besides the components  $XY \dots W$  yet also one or more other components  $MN \dots$  by

$$m \text{ Mol } M + n \text{ Mol } n \dots + x \text{ Mol } X + y \text{ Mol } Y \dots$$

$$+ (1 - m - n \dots - x - y \dots) \text{ Mol } W.$$

We now take in system 31  $q$  quantities of liquid. When the solid

substances take  $\delta w$  quantities of the substance  $W$  from those  $q$  quantities of liquid, then phases-reaction 27 occurs; however, the quantities which participate in this reaction are  $\delta w : \mu$  times as large now. The thermodynamical potential of the solid phases changes by this with:

$$-(\lambda_1 \zeta_1 + \lambda_2 \zeta_2 \dots \lambda_r \zeta_r) \frac{\delta w}{\mu} \dots \dots \dots (32)$$

that of the total liquid  $L$  with

$$\left( -\zeta + m \frac{\partial \zeta}{\partial m} + n \frac{\partial \zeta}{\partial n} \dots + x \frac{\partial \zeta}{\partial x} + y \frac{\partial \zeta}{\partial y} \dots \right) \delta w \dots \dots (33)$$

The total thermodynamical potential of the system 31 changes, therefore, with the sum 32 and 33. As at the equilibrium this change must be zero at constant  $T$  and  $P$  for each reaction possible in the system, the sum of 32 and 33 is zero, therefore, consequently also their sum when the factor  $\delta w$  is omitted. Hence follows that for 30 we may write also:

$$\delta Z_1 = \left( \zeta - m \frac{\partial \zeta}{\partial m} + n \frac{\partial \zeta}{\partial n} \dots - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \dots \right) \mu \dots \dots (34)$$

This means:

the O.W.A. of a system of solid phases between which a phases-reaction may occur by acceptance or loss of the diffusing substance  $W$ , is equal to the O.W.A. of each liquid, with which that system of solid phases can be in equilibrium.

Consequently it follows also from this:

all solutions, which can be in equilibrium with a system of solid substances in which a phases-reaction can occur by acceptance or loss of the diffusing substance  $W$ , have the same O.W.A. and are isotonic, therefore.

The O.W.A. of the system  $Na_2 SO_4 + Na_2 SO_4 \cdot 10 H_2O$  is equal, therefore, to that of each arbitrary liquid  $L$  of the equilibrium:

$$Na_2SO_4 + Na_2SO_4 \cdot 10 H_2O + L \dots \dots \dots (35)$$

Above we have seen that this liquid must contain besides the components  $H_2O$  and  $Na_2 SO_4$  yet at least one other substance. It is indifferent which are those substances or substance f.i. alcohol, acetone,  $KCl$ , sugar etc., provided that only the liquid is in equilibrium with the two solid substances. Consequently an infinite number of liquids exists which may be in equilibrium with  $Na_2 SO_4 + Na_2 SO_4 \cdot 10 H_2O$ ; they are all isotonic.

The same is true also for systems as f.i.  $Na Cl + ice$ ,  $Na_2 SO_4 + ice$  etc. and in general for a system;  $ice + F_2 + F_3 \dots$ ; the phases-reaction which takes place at acceptance or loss of water is then;  $water \rightleftharpoons ice$ .

The preceding properties are deduced in supposition that the phases of system 26 have a constant composition; however, they are valid also for solid substances with a variable composition (f.i. mixed-crystals) and also when one of the phases is gaseous. Consequently they are true also for a system:  $water-vapour + F_2 + F_3 \dots$

From the preceding considerations follow at once the results, which we have deduced in the previous communications for simple cases in ternary systems. Let us take f.i. fig. 2 (Communication V); with the aid of the rule, deduced above sub IV. 1. *a*, we find: the O.W.A. of the solid substance *X* is equal to that of liquid *b*; that of the hydrate *H* is equal to that of liquid *a* and that of the solid mixture *X + Y* is equal to that of liquid *c* (and of course equal also to that of the liquids of the isotonic curves, which go through the points *b*, *a* and *c*).

In fig. 3 (Comm. V) the O.W.A. of the ternary compound *D* is equal to that of liquid *s*, in fig. 4 it is equal to that of the liquid *d*. The O.W.A. of the complex *X + D* is in both figures equal to that of the liquid *d* and that of *Y + D* equal to that of liquid *c*.

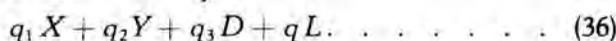
A phases-reaction can occur between the phases *Y + H* in fig. 2 by acceptance and loss of water; with the aid of the rule, deduced sub IV. 3 it follows, that the O. W. A. of *Y + H* is equal to that of liquid *d*.

In the equilibria represented by figs. 3 and 4 (Comm. V) also the complex *X + Y + D* can exist. According to IV. 8 this complex has the same O.W.A. as the liquid in each arbitrary equilibrium:



Of course an infinite number of those equilibria exists, but then the liquid must contain, besides the components *X Y* and *W*, still one or more other components.

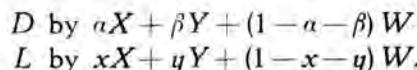
This follows also at once from the figs. 3 and 4; herein viz. no liquid exists, which can be in equilibrium with the three solid substances *X Y* and *D*. Yet in the ternary system itself also liquids exist, which have the same O.W.A. as the complex *X + Y + D*. In order to show this we take an arbitrary system:



in which *q*<sub>1</sub> etc. represent the quantities of the different phases. We take *q* positive and very small with respect to *q*<sub>1</sub> *q*<sub>2</sub> and *q*<sub>3</sub>. As, however, this system (36) is not stable, it passes into the complex:



We now represent the thermodynamical potentials by  $\zeta_x$   $\zeta_y$   $\zeta_D$  and  $\zeta$ , the composition of



With the transition of system (36) into (37) the total thermodynamical potential must decrease; hence follows:

$$\zeta - x \zeta_x - y \zeta_y > (1 - x - y) K \dots \dots \dots (38)$$

in which

$$K = \frac{\zeta_D - a \zeta_x - \beta \zeta_y}{1 - a - \beta} \dots \dots \dots (39)$$

(38) is valid for every arbitrary liquid, therefore, for each value of  $x$  and  $y$ . If we put  $x=0$  and  $y=0$  than (38) passes into  $\zeta_w > K$ , in which  $\zeta_w$  is the thermodynamical potential of water.

We now imagine a liquid  $L$ , which has the same O.W.A. as the complex  $X + Y + D$ ; consequently we have the osmotic equilibrium:

$$\left( X + Y + D \mid L \right) \dots \dots \dots (40)$$

in which the reaction:

$$aX + \beta y - D + (1 - \alpha - \beta) W = 0$$

occurs. The composition  $xy$  of this liquid  $L$  of equilibrium (40) is defined by:

$$\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} = K \dots \dots \dots (41)$$

in which  $K$  has the value, indicated in (39). Now we may always satisfy (41). For  $x=0$  and  $y=0$  the first part of (41) becomes  $\zeta_w$  and, therefore, greater than  $K$ . Let we change  $x$  and  $y$ , then the first part can obtain, therefore, all values between  $\zeta_w$  and  $-\infty$ ; consequently there are also values of  $x$  and  $y$ , for which the first part becomes equal to  $K$ ; consequently we can always satisfy (41). Hence follows, therefore:

in figs. 3 and 4 (Comm. V) is situated anywhere a curve, which represents the solutions, which have the same O.W.A. as the solid complex  $X + Y + D$ .

We are able to deduce something about the position of this isotonic curve. We imagine in those figs. 3 and 4 each of the three saturation-curves to be drawn totally. That of  $D$  then forms a closed curve;  $a c$  then terminates in a point, which we shall call  $c'$ , and  $b d$  in a point which we shall call  $d'$ ; those points  $c'$  and  $d'$  are situated on the side  $XY$ . As the system  $X + Y$  is stable, those curves  $a c c'$  and  $b d d'$  intersect one another in a point  $s'$  within the triangle.

We now can show that the point of intersection of the isotonic curve with the saturation-curve  $a c c' s'$  is situated on the part  $c' s'$ . For this it is sufficient to show that the solution, which is represented by this point of intersection is supersaturated with respect to the solid substance  $X$ .

This solution is defined by the equations:

$$\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} = K \dots \dots \dots (42)$$

$$\zeta - x \frac{\partial \zeta}{\partial x} + (1 - y) \frac{\partial \zeta}{\partial y} = \zeta_y \dots \dots \dots (43)$$

the first of which represents the isotonic curve and the second one the saturation-curve of the solid substance  $Y$ . We find from this:

$$\zeta + (1 - x) \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} - \zeta_x = \frac{\zeta - x \zeta_x - y \zeta_y - (1 - x - y) K}{x} \dots (44)$$

We find this by substituting in the first part of (44) f.i. the values of  $\frac{\partial \zeta}{\partial x}$  and  $\frac{\partial \zeta}{\partial y}$ , which follow from (42) and (43). When the first part should be zero, then this meant that the liquid was in equilibrium with the solid substance  $X$ . According to (38) the second part of (44) is positive, however; this means that the liquid is supersaturated with respect to the solid substance  $X$ .

Generally we are able to prove now that all liquids of the isotonic curve are supersaturated; consequently this curve is situated totally within the supersaturated region.

The O.W.A. of the solid complex  $X + Y + D$  is, therefore, greater than those of the liquids  $c$  and  $d$  (figs. 3 and 4 comm. V) and those of all other saturated and unsaturated liquids. When we bring the solid complex in osmotic contact with one of those saturated or unsaturated liquids, then it takes water in and passes into one of the equilibria  $X + D + \text{liquid } d$  or  $Y + D + \text{liquid } c$ .

*(To be continued).*

*Leiden, Lab. of Inorg. Chemistry.*

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**Chemistry.** — “Equilibria in systems in which phases, separated by a semipermeable membrane.” VII. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of March 28, 1925).

*Osmotic equilibria and -complexes; the membrane-phase-rule.*

We take an osmotic system:

$$E = \left[ E_1 (n_1 r_1) \mid E_2 (n_2 r_2) \right] \dots \dots \dots (1)$$

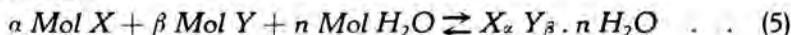
in which  $E_1$  consists of  $n_1$  components in  $r_1$  phases and  $E_2$  of  $n_2$  components in  $r_2$  phases. Let us take as examples the systems:

$$\left( L \mid L_1 \right) ; \left( X + L \mid L_1 \right) ; \left( X + Y + L \mid L_1 \right) \dots (2)$$

$$\left( X + X \cdot n H_2O \mid L \right) \dots \dots \dots (3)$$

$$\left( X + Y + X_\alpha Y_\beta \cdot n H_2O \mid L \right) \dots \dots \dots (4)$$

in which  $L$  and  $L_1$  represent aqueous liquids. If water is the diffusing substance, then a little water may diffuse from right to left and reversally, without a new phase is formed or an existing phase disappears totally. This is always the case when a liquid occurs on both sides of the membrane, as in the systems (2). In the systems (3) and (4) a reaction takes place on the left side on taking in or losing water; this reaction is for system (4):



Let us take now the systems:

$$\left( X \mid L \right) ; \left( X \cdot n H_2O \mid L \right) \dots \dots \dots (6)$$

$$\left( X + Y \mid L \right) \dots \dots \dots (7)$$

$$\left( X + X_\alpha Y_\beta \cdot n H_2O \mid L \right) \dots \dots \dots (8)$$

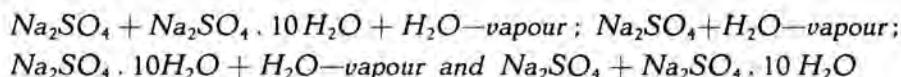
In system (7) and in the first one of the systems (6) no water can diffuse from left to right; if water diffuses from right to left, then on the left side a new phase must arise, f.i. a liquid, a hydrate or water-vapour.

In system (8) and the second one of the systems (6) water is present as well at the right as at the left side of the membrane; with diffusion

of water, independent in which direction, a new phase must be formed at the left side.

Consequently, diffusion of a little water causes in the systems (6)—(8) always the occurrence of one or more new phases, so that the system totally changes its character; in the systems (2)—(4), however, only a small change occurs either in the quantities or in the compositions of the phases, which exist already.

For this reason we shall say that the systems (2)—(4) are osmotic equilibria and the systems (6)—(8) complexes. This may be compared f. i. with the systems:



the first one of which is an equilibrium, but the other three are only complexes, in which nothing may take place without a new phase is formed.

We now take the case that there are two diffusing substances f. i. water and the substance *Y*. Then the systems (2) and (4) are in osmotic equilibrium with respect to both the diffusing substances. Small quantities of water and *Y* viz. may diffuse, independent from one another, in both directions, without a new phase is occurring. System (3), however, is only in osmotic equilibrium with respect to water, but not with respect to *Y*.

The systems (6) are, neither with respect to water, nor with respect to *Y*, osmotic equilibria, but complexes; system (7) is a complex with respect to water, but an osmotic equilibrium with respect to *Y*.

System (8) shows something particular; this is viz. a complex, as well with respect to water only as with respect to *Y* only. If, however, both substances diffuse in a definite ratio viz.  $n \text{ Mol. } H_2O : \beta \text{ Mol. } Y$ , then reaction (5) may occur and the complex behaves like an osmotic equilibrium; we will call it preliminarily osmotic.

Consequently we find: with respect to both the diffusing substances the osmotic system can be:

- either a complex (system 6)
- or an osmotic equilibrium (systems 2 and 4)
- or a preliminarily osmotic equilibrium (system 8)
- or a complex with respect to the one diffusing substance and an osmotic equilibrium with respect to the other diffusing substance (systems 3 and 7).

If three or more diffusing substances occur, then similar cases may be distinguished.

*The membrane-phase-rule.*

We take the osmotic equilibrium:

$$E = E_1(n_1 r_1) | E_2(n_2 r_2) \dots \dots \dots (9)$$

in which  $E_1$  consists of  $n_1$  components in  $r_1$  phases under a pressure  $P_1$  and  $E_2$  of  $n_2$  components in  $r_2$  phases under a pressure  $P_2$ . The phase-rule of GIBBS is valid for each of the two systems separately; therefore, at constant temperature  $E_1$  has  $n_1 - r_1 + 1$  freedoms and  $E_2$  has  $n_2 - r_2 + 1$  freedoms; consequently the total system has  $n_1 + n_2 - (r_1 + r_2) + 2$  freedoms.

When  $E_1$  and  $E_2$  are in osmotic equilibrium with one another with respect to the diffusing substance  $W$ , then, as we have seen in the previous communication, there is an equation, which expresses that the O.W.A. of  $E_1$  is equal to that of  $E_2$ . The total number of freedoms is diminished, therefore, with one.

When  $E_1$  and  $E_2$  are in osmotic equilibrium with respect to  $d$  diffusing substances, then there are  $d$  equations; the total number of freedoms is diminished, therefore, with  $d$ .

Consequently we may say:

the number of freedoms of an osmotic equilibrium:

$$E_1(n_1 r_1) | E_2(n_2 r_2)$$

in which  $d$  diffusing substances occur, is at constant temperature:

$$n_1 + n_2 - (r_1 + r_2) + 2 - d \dots \dots \dots (10a)$$

consequently equal to the sum of the freedoms of both systems separately, diminished with the number of diffusing substances.

If we take also the temperature variable, then the number of freedoms becomes:

$$n_1 + n_2 - (r_1 + r_2) + 3 - d \dots \dots \dots (10b)$$

We shall apply this to some of the systems, formerly discussed. Let us take f.i. the osmotic equilibrium:

$$E = \left( \text{water} | L \right) \dots \dots \dots (11)$$

in which water is the diffusing substance and  $L$  a binary liquid. At constant temperature the left system has one freedom and the right one has two freedoms. As there is one diffusing substance, the total system has  $1 + 2 - 1 = 2$  freedoms, therefore.

We now give to the water a definite pressure  $P_0$ , so that one freedom disappears; consequently the total system has still one freedom. Therefore to each concentration of the liquid  $L$  belongs a definite pressure  $P$  and consequently also a definite osmotic pressure  $P - P_0$  of this liquid.

Let us take the osmotic equilibrium:

$$E = L_1 | L_2 \dots \dots \dots (12)$$

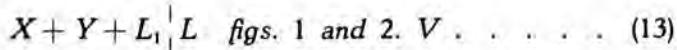
with one diffusing substance f.i. water; we assume that both liquids are

ternary. If we keep temperature and pressure constant (the pressure may be for both liquids equal or different) then each liquid has 2 freedoms; the total system has, therefore,  $2 + 2 - 1 = 3$  freedoms.

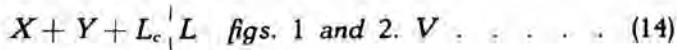
If we take for  $L_1$  a liquid of definite composition, then 2 freedoms disappear; consequently  $L_2$  has still one freedom; it is represented, therefore, in a diagram by a curve. If both liquids have the same pressure and if they consist of the same components, then this is the isotonic curve, formerly discussed, which goes through the point, representing liquid  $L_1$ .

We now take some equilibria, which are represented in the figures of the communications III—V. In order to remain in accordance with those diagrams, we assume that there is one diffusing substance viz.  $W =$  water and that the pressure of both the separate systems is equal and constant.

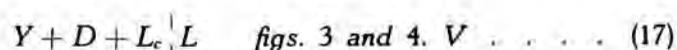
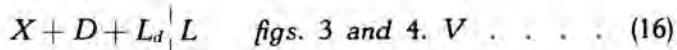
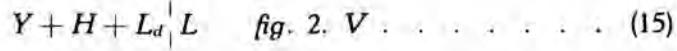
In the osmotic equilibrium:



the left system has no more a freedom, as  $T$  and  $P$  are constant; liquid  $L_1$  must have, therefore, a definite composition viz.  $c$ ; we represent it by  $L_c$ . (13) becomes, therefore:

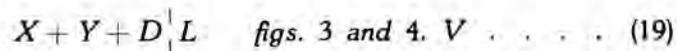
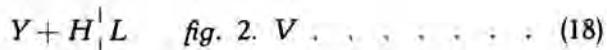


Also in the osmotic equilibria:



the liquids on the left side of the membrane must have the indicated composition. As the systems (14)—(17) are osmotic equilibria with one diffusing substance, as the left system is zero and the right one has two freedoms, the total number becomes, therefore,  $0 + 2 - 1 = 1$  freedom. Consequently the liquid  $L$  is monovariant ( $P.T$ ) and is represented, therefore, by a curve. In system (14) this is the isotonic curve, not-drawn, going through point  $c$ , all points of which, except point  $c$  itself, represent metastable liquids; in system (15) this is the isotonic curve  $dn$  (and its metastable prolongation), etc.

Also the systems:



are osmotic equilibria. As in each of those equilibria the system at the left side of the membrane has no freedom, each of those equilibria has, therefore,  $0 + 2 - 1 = 1$  freedom. The liquid  $L$  is, therefore, monovariant ( $P.T$ ) again and is represented by the points of a curve. In (18) this is the same as in (15) viz. curve  $dn$ ; in (19) this is, as we have previously seen, a curve, all points of which represent metastable states.

We now take the osmotic equilibrium:

$$Y + L_1 \Big| L \quad \text{figs. 1, 2 and 3. III} \quad \dots \quad (20)$$

in which of course  $L_1$  represents a liquid of  $wv$ , viz. of the saturation-curve of  $Y$ . As the left system has one freedom and the right one two freedoms, the total equilibrium has, therefore,  $1 + 2 - 1 = 2$  freedoms; consequently it is divariant ( $P.T$ ). If we take for  $L_1$  a definite liquid  $L_a$  of the saturation-curve, then one freedom disappears; consequently liquid  $L$  has still one freedom. It is represented, therefore, by the points of the isotonic curve  $an$ . We shall represent those liquids by  $L(1-an)$ , in which the 1 indicates that the liquids have one freedom and  $an$  is, therefore, a curve. Then we may represent the equilibrium by

$$Y + L_a \Big| L(1-an) \quad \text{figs. 1, 2 and 3. III} \quad \dots \quad (21)$$

As we may take for  $L_1$  in (20) each arbitrary liquid of curve  $wv$ , we have a.o. also the following equilibria:

$$Y + L_w \Big| L(1-wm) \quad ; \quad Y + L_b \Big| L(1-bo); \text{ etc.} \quad \dots \quad (22)$$

which represent, therefore, just as (21) special cases of (20).

For the osmotic equilibria

$$H + L_1 \Big| L \quad \text{fig. 1. IV} \quad \dots \quad (23)$$

$$D + L_1 \Big| L \quad \text{fig. 2. IV} \quad \dots \quad (24)$$

the same is valid as for (20). Special cases of (23) are a.o:

$$H + L_w \Big| L(1-wm) \quad ; \quad H + L_c \Big| L(1-ncn'); \text{ etc.}$$

and of (24):

$$D + L_w \Big| L(1-mwm') \quad ; \quad D + L_f \Big| L(1-nfan'); \text{ etc.}$$

The osmotic system:

$$Y \Big| L \quad \text{fig. 1. III} \quad \dots \quad (25)$$

is not an equilibrium, but an osmotic complex; as the diffusing substance does not change, therefore, the number of freedoms, this complex has

$0 + 2 = 2$  freedoms. Consequently liquid  $L$  is bivariant ( $P.T$ ) and is represented by the points of a field.

We are able to find the position of this field in the following way. We imagine in (25) the substance  $Y$  in equilibrium with a liquid of the saturation-curve  $wv$ , f. i. with the liquid  $a$ . We then get equilibrium (21). If we take away from this the liquid  $L_a$ , then remains the complex:

$$Y \mid L(1-am) \quad \text{fig. 1. III} \quad \dots \quad (26)$$

The solid substance  $Y$  can exist, therefore, in osmotic contact with the liquids of curve  $am$ ; consequently this curve must be situated in the field of the liquid  $L$  in (25), which is wanted. If we substitute  $L_a$  in (21) by  $L_w$  or  $L_b$  then we get the equilibria (22); the curves  $wm$  and  $bo$  are situated, therefore, also in the field wanted.

As we may substitute  $L_a$  in (21) by any arbitrary liquid of curve  $wv$ , all isotonic curves, going through a point of curve  $wv$ , are situated, therefore, in the field. Those curves define a field, which we shall represent by  $L(2-wmXv)$ ; the 2 indicates that the liquids have 2 freedoms and that  $wmXv$  is a field, therefore. The wanted field of (25) therefore, must either coincide with the field  $wmXv$  or extend itself over it. Further we shall see that it coincides with it. Therefore, the osmotic system (25) is defined more closely by:

$$Y \mid L(2-wmXv) \quad \text{fig. 1. III} \quad \dots \quad (27)$$

Consequently we find, in accordance with our previous considerations: the solid substance  $Y$  may be in osmotic contact with the liquids of the field  $wmXv$  without taking water from those liquids. Also we may say, therefore:

the  $O.W.A.$  of the solid substance  $Y$  is smaller than that of the liquids of the field  $wmXv$ .

In a similar way we find the fields of other osmotic complexes f. i.

$$Y \mid L(2-ambc) \quad \text{fig. 1. V} \quad \dots \quad (28)$$

$$Y \mid L(2-dnbc) \quad \text{fig. 2. V} \quad \dots \quad (29)$$

$$H \mid L(2-wm\circ v) \quad \text{fig. 1. IV} \quad \dots \quad (30)$$

$$H \mid L(2-amnd) \quad \text{fig. 2. V} \quad \dots \quad (31)$$

$$D \mid L(2-mwm'p'vp) \quad \text{fig. 2. IV} \quad \dots \quad (32)$$

Hence appears that the liquids which may be in osmotic contact with

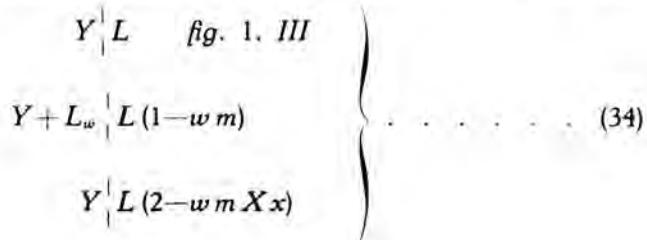
the solid substance, without waterdiffusion, are divariant; they are situated in the indicated field.

We are able to deduce those fields also in the following way. We take the osmotic complex:



We take in the field, sought for, an arbitrary liquid  $L_x$ ; as no water diffuses from this towards  $Y$ , the O.W.A. of  $L_x$  is greater, therefore, than that of the solid substance  $Y$ . As  $L_x$  changes its place in the field, then it alters its O.W.A., if not, it proceeds along an isotonic curve. We now imagine that  $L_x$  changes its place in such a way that its O.W.A. becomes smaller constantly f. i. at a displacement along a straight line in the direction of point  $W$ . At a definite composition of  $L_x$  its O.W.A. then becomes equal to that of  $Y$  and in (33) a little water may diffuse from  $L_x$  towards  $Y$ . On the left side of the membrane is then formed a little of the liquid  $L_w$ ; liquid  $L_x$  is represented then by a point of the isotonic curve  $w m$ .

If  $L_x$  is displaced still further towards point  $W$ , then its O.W.A. becomes smaller perpetually, then the osmotic complex (33) can exist no more. The field sought for is situated, therefore, at the right of curve  $w m$  and is, therefore, the field  $w m X Y$  or, if we limit ourselves to the stable part, the field  $w m X v$ . We shall represent a similar deduction by:



Firstly viz. we write the osmotic complex, the field of which we wish to define, then the osmotic equilibrium which arises with diffusion of a little water and at last the osmotic equilibrium, mentioning the field found.

For the field of the osmotic complex



we find 2 limit-curves. If a liquid proceeds along a straight line towards the point  $W$ , then it gives at a definite composition water to  $H$ , so that this passes into  $H + L_a$ ; if this liquid proceeds along the straight line in opposite direction, then its O.W.A. increases and it takes water from  $H$

at a definite composition; this then passes into  $Y + H$ . We now represent this in a similar way as in (34) viz.

$$\left. \begin{array}{l} H \mid L \quad \text{fig. 2. V} \\ H + L_a \mid L(1-am) \mid Y + H \mid L(1-dn) \\ H \mid L(2-amnd) \end{array} \right\} \dots \dots \dots (36)$$

The only difference with (34) is that with diffusion of water, now two different osmotic equilibria may occur; at the left side of the line we write the equilibrium, which arises at diffusion of a little water towards the left, at the right side of the line the equilibrium, which arises at diffusion of a little water towards the right. This result is in accordance with that in (31). We now may say:

the hydrate  $H$  can be in osmotic contact with the liquids of the field  $amnd$  without it is taking water from those liquids or reversally without it is giving water to them. Liquids, at the left of this field, give water to the hydrate; liquids at the right of this field, take water from the hydrate.

In a similar way we find a.o.:

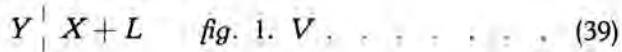
$$\left. \begin{array}{l} H \mid L \quad \text{fig. 1. IV} \\ H + L_w \mid L(1-wm) \mid H + L_v \mid L(1-vo) \\ H \mid L(2-wm \circ v) \end{array} \right\} \dots \dots \dots (37)$$

which is in accordance with (30)

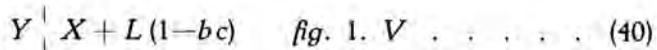
$$\left. \begin{array}{l} X + Y \mid L \quad \text{fig. 1 or 2. V} \\ X + Y + L_c \mid L(1-c'c'') \\ X + Y \mid L(2-c'c''XY) \end{array} \right\} \dots \dots \dots (38)$$

Herein the isotonic curve (not drawn in the figure) going through point  $c$  is represented by  $c'c''$ . The liquids of the field are all supersaturated. As all saturated and unsaturated liquids are situated outside this field, they shall give water to the solid mixture  $X + Y$ . We may also say, therefore: the O.W.A. of solid  $X + Y$  is greater than that of all saturated and unsaturated liquids.

We now take the osmotic complex:

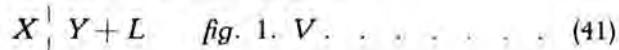


in which a solid substance is on both sides of the membrane. As the liquid is saturated with solid  $X$ ,  $L$  in (39) can be represented only by points of curve  $bc$ . As the *O.W.A.* of the solid substance  $Y$  is equal to that of the liquids of curve  $am$ , the *O.W.A.* of the solid substance  $Y$  is also smaller, therefore, than that of all liquids of curve  $bc$ . Consequently we may write for (39):

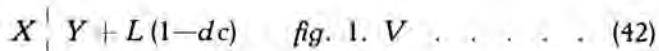


Therefore, the solid substance  $Y$  may be in osmotic contact with all liquids, which are saturated with solid  $X$ , without taking water from those liquids.

Otherwise it is, however, in the osmotic complex:



in which the liquids, saturated with  $Y$  are represented by points of curve  $ac$ . The *O.W.A.* of the substance  $X$  is equal to that of the liquids of curve  $bd$ ; consequently point  $d$  divides curve  $ac$  into two parts; as the liquids of part  $dc$  have a greater *O.W.A.* than that of liquid  $d$  and, therefore, also a greater *O.W.A.* than the solid substance  $X$ , we may write for (41):



Consequently the solid substance  $X$  cannot be in osmotic contact with all liquids, saturated with solid  $Y$ , but only with the liquids, which are represented by part  $dc$  of the saturation-curve; if we bring in osmotic contact solid  $X$  with liquids of part  $ad$  of this saturation-curve, then  $X$  shall flow away totally or partially.

(To be continued).

Leiden, Lab. of Inorg. Chemistry.

**Chemistry.** — “*In-, mono- and plurivariant equilibria*” XXIX. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of March 28, 1925).

*Influence of one or more new substances on an equilibrium, in which a phases-reaction may occur.*

In the communications XX—XXIII we have discussed already the influence of one new substance on in- and monovariant equilibria; now we shall discuss some more general cases.

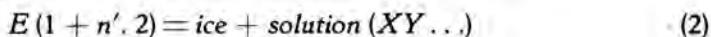
We take an equilibrium  $E(n, r)(r)$ , consequently an equilibrium of  $n$  components in  $r$  phases, in which a phases-reaction can occur between these  $r$  phases. If  $r < n + 1$ , then those phases have to satisfy definite conditions; if  $r = n + 1$ , then this is not necessary. In communication XXVI we have discussed those equilibria  $E(n, r)(r)$ ; they are monovariant and are represented in a  $PT$ -diagram by a curve.

By addition of  $n'$  new substances to the equilibrium  $E(n, r)(r)$  a new equilibrium of  $n + n'$  components in  $r$  phases arises; as generally no phases-reaction shall occur now between the  $r$  phases, the new equilibrium is an equilibrium  $E(n + n', r)$ . Only under definite conditions this can form, as we shall see later, an equilibrium  $E(n + n', r)(r)$ .

Firstly we shall briefly indicate some examples. If we add to the equilibrium

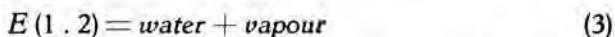


$n'$  new substances  $XY$  etc., then arises the equilibrium:



in which  $(XY \dots)$  indicates that the solution contains, besides the original component (viz. water) yet also the new substances  $XY$  etc.

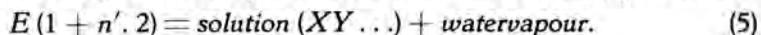
If we add to the equilibrium:



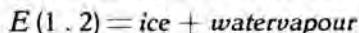
$n'$  new substances, which are all volatile, then arises the equilibrium:



If one or more of the new substances are not volatile, then they disappear in the vapour; if they all are not volatile, then (4) passes into:



We may add also  $n'$  volatile substances to the equilibrium



so that it passes into

$$E(1 + n'. 2) = \text{ice} + \text{vapour} (XY \dots) \quad (6)$$

Of course the same is also true if we replace in the previous equilibria the component water by benzene, naphthalene etc.

If we have f.i. the equilibrium:

$$E(1. 2) = \text{solid benzene} + \text{liquid benzene} \quad (7)$$

then this can, when the new substances form mixed-crystals with benzene, pass into:

$$E(1 + n'. 2) = \text{mixed-crystal} (XY \dots) + \text{solution} (XY \dots). \quad (8)$$

Of course also one or more of the new substances can be missing in the mixed-crystal.

If we add to the equilibria:

$$E(2. 3) = \text{solution} + Na_2SO_4 \cdot 10 H_2O + Na_2SO_4 \quad (9)$$

$$E(2. 3) = \text{watervapour} + Na_2SO_4 \cdot 10 H_2O + Na_2SO_4 \quad (10)$$

$n'$  new substances, then they may pass into:

$$E(2 + n'. 3) = \text{solution} (XY \dots) + Na_2SO_4 \cdot 10 H_2O + Na_2SO_4 \quad (11)$$

$$E(2 + n'. 3) = \text{vapour} (XY \dots) + Na_2SO_4 \cdot 10 H_2O + Na_2SO_4 \quad (12)$$

With this still also mixed-crystals might be formed with one or both solid phases.

In the equilibria:

$$E(n. 2)(2) = \text{liquid} + \text{vapour} \quad (13)$$

$$E(n. 2)(2) = \text{liquid} + \text{mixed-crystal} \quad (14)$$

the two phases have, therefore, the same composition; on addition of  $n'$  new substances they pass into:

$$E(n + n'. 2) = \text{liquid} (XY \dots) + \text{vapour} (XY \dots) \quad (15)$$

$$E(n + n'. 2) = \text{liquid} (XY \dots) + \text{mixed-crystal} (XY \dots) \quad (16)$$

In the mixed-crystals and in the vapour one or more or all new substances may miss.

The equilibria  $E(n. n+1)$  and  $E(n. r)(r)$ , indicated here, are represented in a  $PT$ -diagram by a curve; consequently a definite pressure  $P_q$  belongs to a definite temperature  $T_q$  and reversally. On addition of the new substances temperature and pressure will be able to change; as we shall see further, we may also keep constant either the temperature or the pressure. Firstly we shall discuss the latter case.

*Influence of one or more new substances under constant pressure  
on an equilibrium, in which a phases-reaction may occur.*

If we add to an equilibrium  $E(n. r)(r)$  under constant pressure  $P_q$  the

$n'$  new substances, so that an equilibrium  $E(n + n'.r)$  arises, then the temperature will change. Three cases may occur now, viz.

- the temperature increases
- the temperature decreases

or the temperature increases or decreases or rests unchanged, dependent on the mutual ratio of the new substances.

Although generally without closer examination it is not possible to know, which of those three cases shall occur, yet it is possible in some cases to make a conclusion by a simple discussion.

From the equilibrium  $E(n.r)(r)$  may be formed viz. by addition or withdrawal of heat equilibria, in which one or more of the original phases are missing. When we consider the equilibrium  $E(n.r)(r)$  under constant pressure at a temperature  $T_q$ , then the equilibria which are formed with addition of heat, will be constant at higher temperatures; those which are formed on withdrawal of heat are constant at temperatures lower than  $T_q$ .

Consequently we are able to define for each equilibrium  $E(n.r)(r)$  which groups of phases exist at temperatures higher than  $T_q$  and which groups at temperatures lower than  $T_q$ . Let us take f.i. the equilibrium (1); as water arises on addition of heat and ice at withdrawal of heat, the water, therefore, shall exist above  $0^\circ$  and the ice below  $0^\circ$  under a pressure of one atmosphere.

We now add to the equilibrium:

$$E(n.r)(r) = L_0 + M_0 + N_0 \dots + Q_0 + R_0 \dots \dots \dots (17)$$

the  $n'$  new substances, so that it passes into an equilibrium:

$$E(n + n'.r) = L + M + N \dots + Q + R \dots \dots \dots (18)$$

the phases of which differ little from those of the equilibrium (17). If we add only one of the new substances f.i.  $X$  or  $Y$ , then we shall represent the new equilibrium by  $E(X)$  or  $E(Y)$ ; if we add the three new substances  $XY$  and  $Z$ , we represent it by  $E(XYZ)$ ; etc.

We now add the new substance  $X$  only, so that (18) is an equilibrium  $E(X)$ . In case the new substance does not appear in all phases, we shall divide the phases of (18) into two groups; by  $[X]$  we represent the group in which the new substance  $X$  occurs; by  $[o]$  the group, in which the new substance  $X$  does not occur. Consequently we write for (18):

$$E(X) = [o] + [X] \dots \dots \dots (19)$$

This equilibrium can only exist at the temperatures at which the phases-group  $[o]$  is constant; as this is known, in accordance with the discussed above, we know also, therefore, the temperatures at which the equilibrium  $E(X)$  might exist.

As the same is also true for equilibria  $E(Y), E(Z), E(XY)$  etc., it follows:

- a. if the new substances are missing in one or more of the phases,

then the new equilibrium can exist only at temperatures, at which the phases-group, which is formed by the phases, in which those new substances are missing, is constant.<sup>1)</sup>

*b.* if the new substances occur only in one or more of the phases, which arise at the phases reaction

on addition of heat, then the temperature decreases

on withdrawal of heat, then the temperature increases.

Later we shall deduce this in another way also.

We now shall apply those considerations to some examples. If we add to the equilibrium (1) the  $n'$  new substances, so that the equilibrium:

$$E(1 + n'. 2) = \text{ice} + \text{solution}(XY \dots)$$

arises, then the temperature shall decrease. The new substances do not occur viz. in the ice; according to (*a*) the new equilibrium can exist, therefore, only at temperatures at which the ice exists, consequently (under a pressure of 1 atmosphere) below  $0^\circ$ . This also follows with the aid of (*b*); the new substances viz. occur in the water only, therefore, in the phase, which is formed in (1) on addition of heat; consequently the temperature is lowered.

In the same way it appears that the equilibrium:

$$E(1 + n'. 2) = \text{solution}(XY \dots) + \text{water-vapour}$$

which arises by addition of  $n'$  substances, which are not volatile, to the equilibrium (3), exists at higher temperatures than equilibrium (3). Consequently the boiling-point of the liquid is raised. We find in this way:

addition of one or more new substances lowers the melting-point and the sublimation-point of solid substances;

addition of new substances, which are not volatile, raises the boiling-point of a liquid.

If the new substances, which we add to equilibrium (3) are volatile, so that an equilibrium:

$$E(1 + n'. 2) = \text{solution}(XY \dots) + \text{vapour}(XY \dots)$$

arises, then, of course, we cannot apply the rules *a* and *b*. Later we shall see in which way we can find also in this case the change in temperature.

If, however, one of the new substances f. i.  $X$  is not volatile, so that an equilibrium:

$$E(1 + n'. 2) = \text{solution}(XY \dots) + \text{vapour}(Y \dots)$$

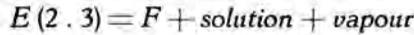
arises, then we may conclude anything again. If we omit viz. the volatile substances  $Y$  etc. then we get an equilibrium:

$$E(X) = \text{solution}(X) + \text{watervapour},$$

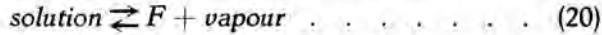
<sup>1)</sup> Compare also communication XXVII of this series.

so that the boiling point of the liquid is raised by addition of the new substance  $X$ . However, it rests yet unknown which influence the other substances and their mixtures with  $X$  will have on the boiling-point.

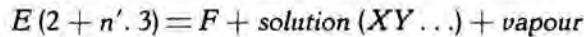
Let us take the binary equilibrium:



in which  $F$  is a solid substance. We assume that the phases-reaction:



occurs and that this reaction takes place from left to right on addition of heat. If we add  $n'$  substances, which are not volatile, then arises the equilibrium:

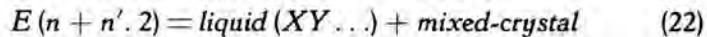
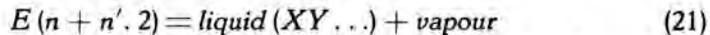


so that the known substances do not occur in the phases-group  $F + \text{vapour}$ ; according to reaction (20) this group exists at higher temperatures; according to (a) addition of the new substances will cause, therefore, increase of the temperature. The same follows also with the aid of (b); the new substances occur viz. only in the solution and this arises, according to (20) on withdrawal of heat.

We may apply those considerations also to equilibria, which consist of one liquid and further of solid substances. The temperature, at which such an equilibrium occurs, may be called the common melting- or inversion-point of those substances. We now assume that heat must be added for the formation of liquid at the phases-reaction; then we find:

the common melting- or inversion-point of a mixture of solid substances is lowered by the addition of new substances, if those occur in the liquid only.

We add to the equilibria (13) and (14) new substances, which occur in the liquid only; we then get the equilibria:



Let us call the composition of the vapour in equilibrium (13)  $G_0$  and that of the mixed-crystals in (14)  $M_0$ . The vapour, which is formed, on increase of  $T$  from equilibrium (13) shall, therefore, have also the composition  $G_0$ ; and the mixed-crystal, which is formed on decrease of  $T$  from equilibrium (14) will have the composition  $M_0$ .

In the equilibria (21) and (22) vapour and mixed-crystal may have, however, an infinite number of compositions, which differ from  $G_0$  and  $M_0$ . Consequently it is not allowed to apply the former rules without more, to all the equilibria (21) and (22); it is allowed, however, if we choose from the infinite number of equilibria, those, in which the vapour has the composition  $G_0$  and the mixed-crystal the composition  $M_0$ . Consequently we may conclude that of all equilibria (21) surely one exists at higher temperatures and of all equilibria (22) surely one at lower

temperatures. An examination more in detail may, as we shall see further, decide with regard to the other equilibria.

In order to elucidate the previous general considerations further, we represent the phases-reaction, which may take place in the equilibrium:

$$E(n, r)(r) = L_0 + M_0 + N_0 \dots + Q_0 + R_0 \dots \dots \dots (23)$$

between the  $r$  phases by:

$$\varrho_1 L_0 + \varrho_2 M_0 + \varrho_3 N_0 \dots + \varrho_r R_0 = 0 \dots \dots \dots (24)$$

so that  $\Sigma(\varrho) = \varrho_1 + \varrho_2 \dots + \varrho_r = 0$ . Consequently we are able to express one of the phases f.i.  $L_0$  in the  $r-1$  other ones viz.

$$L_0 = a_1 M_0 + a_2 N_0 + \dots + a_{r-1} R_0 \dots \dots \dots (25)$$

in which  $\Sigma(a) = a_1 + a_2 \dots a_{r-1} = 1$ . From (24) and (25) follow the relations:

$$\varrho_1 a_1 + \varrho_2 = 0 \quad \varrho_1 a_2 + \varrho_3 = 0 \dots \varrho_1 a_{r-1} + \varrho_r = 0 \dots \dots (26)$$

in which  $\Sigma(\varrho) = 0$  is included.

In order to represent an equilibrium, the phases of which differ a little from those of the equilibrium (23), we have to take  $n$  composants; for this we take the  $r-1$  phases  $M_0 \dots R_0$  and further still  $n-r+1$  arbitrary phases  $U V$  etc. In order to represent the equilibrium:

$$E(n + n', r) = L + M + N \dots + Q + R \dots \dots \dots (27)$$

we need still  $n'$  new composants; for this we take the  $n'$  new substances  $XY$  etc. We now can represent an arbitrary phase  $F$  of the equilibrium (27) by:

$$F = xX + yY \dots + uU \dots + mM_0 + nN_0 \dots + qQ_0 + rR_0 \dots (28)$$

in which we take  $r = 1 - x \dots - q$ . In order to represent the  $r$  phases of the equilibrium (27) we give in (28) to the variables successively the indices  $1, 2 \dots r$ .

If we put further:

$$\zeta - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \dots - u \frac{\partial \zeta}{\partial u} \dots - m \frac{\partial \zeta}{\partial m} - n \frac{\partial \zeta}{\partial n} \dots - q \frac{\partial \zeta}{\partial q} = \varphi \dots (29)$$

then for the equilibrium (27) the  $r-1$  equations:

$$\varphi_1 = \varphi_2 = \dots = \varphi_{r-1} = \varphi_r \dots \dots \dots (30)$$

are true.

We find  $\varphi_1 \varphi_2$  etc. by giving in (29) to all letters successively the indices  $1, 2 \dots r$ .

Further we still have the equations:

$$\left(\frac{\partial \zeta}{\partial x}\right)_1 = \left(\frac{\partial \zeta}{\partial x}\right)_2 = \dots = \left(\frac{\partial \zeta}{\partial x}\right) \dots \dots \dots (31)$$

and those, which follow herefrom, if we replace  $x$  successively by the

other variables of (28). Consequently in (31) we find  $n + n' - 1$  series, each of  $r - 1$  equations; therefore, together  $(n + n' - 1)(r - 1)$  equations. Consequently we have in total  $(n + n')(r - 1)$  equations; if we keep the pressure constant, then there are  $(n + n' - 1)r + 1$  equations; therefore, equilibrium (27) has  $n + n' - r + 1$  equations. If  $r = n + 1$ , as in the examples 1-12, then the number of freedoms becomes  $n'$ , consequently equal to the number of new substances, which are added.

If the equilibrium  $E(n, r, r)$  exists at the temperature  $T_q$  then we consider the equilibrium  $E(n + n', r)$  at the temperature  $T_q + \Delta T$ ; further we assume that the phases of both equilibria differ only very little from one another.

In (29) and (31)  $\frac{\partial \zeta}{\partial x}, \frac{\partial \zeta}{\partial y}$  etc. which refer to the new components, get infinitely large; for this we put:

$$\zeta = \zeta' + RT(x \log x + y \log y + \dots) \dots \dots (32)$$

in which we take between parentheses only the variables of the  $n'$  new substances. From this follow a. o. the equations:

$$\left. \begin{aligned} \frac{\partial \zeta}{\partial x} = \frac{\partial \zeta'}{\partial x} + RT(1 + \log x) \quad \frac{\partial \zeta}{\partial y} = \frac{\partial \zeta'}{\partial y} + RT(1 + \log y) \\ - \eta = \frac{\partial \zeta'}{\partial T} + R(x \log x + y \log y + \dots) \end{aligned} \right\} \dots (33)$$

With the aid of those equations the  $n'$  first series of the equations (31) pass into:

$$\left. \begin{aligned} \frac{x_1}{a_1} = \frac{x_2}{a_2} = \dots = \frac{x_r}{a_r} \\ \frac{y_1}{\beta_1} = \frac{y_2}{\beta_2} = \dots = \frac{y_r}{\beta_r} \end{aligned} \right\} \dots \dots \dots (34)$$

etc. For infinitely small values of those variables the denominators (viz. the  $r - 1$  ratios in each series) approach to definite values.

Hence follows:

the division of the new substances  $XY$  etc. over the  $r$  phases of the equilibrium  $E(n + n', r)$  is not arbitrary. The division of substance  $X$  is defined by the first series of the equations (34); that of substance  $Y$  by the second series etc.

If, therefore, we know the quantity of one of the new substances f.i. of  $X$  in one of the  $r$  phases, then, in accordance with (34) we know also the quantity of this substance  $X$  in each of the other  $r - 1$  phases.

The  $n - 1$  other series of (31) become:

$$\Delta \left( \frac{\partial \zeta}{\partial u} \right)_1 = \Delta \left( \frac{\partial \zeta}{\partial u} \right)_2 = \dots = \Delta \left( \frac{\partial \zeta}{\partial u} \right)_r \dots \dots (35)$$

and still  $n - 2$  other series. The sign  $\Delta$  indicates with this that we have to differentiate with respect to all variables, also  $T$ .



so that we may write also:

$$\Sigma \varrho (x + y \dots) = \Sigma (\varrho x) + \Sigma (\varrho y) + \dots$$

Each of those terms  $\Sigma (\varrho x)$ ,  $\Sigma (\varrho y)$ , etc. contains, on account of the equations (34), only one independent variable.

Firstly we put  $r = n + 1$  so that the equilibrium has  $n'$  freedoms. We now are able to satisfy the equations by taking all variables of the same order; (40) then passes into:

$$(\Delta T)_p = - \frac{RT_q}{\Sigma (\varrho \eta)} \cdot \Sigma \varrho (x + y \dots) \dots \dots \dots (41)$$

or

$$(\Delta T)_p = - \frac{RT_q}{\Sigma (\varrho \eta)} [\Sigma (\varrho x) + \Sigma (\varrho y) \dots] \dots \dots (42)$$

in which  $(\Delta T)_p$  indicates that the change in  $T$  takes place under constant pressure. This change in  $T$  depends, therefore, only on the quantities of the new substances  $X Y$  etc. in the different phases.

We now let the phases-reaction (24) take place in such direction that the entropy increases; then  $\Sigma (\varrho \eta)$  is positive. The phases, which are formed with this reaction, then have a positive coefficient in (24); the phases which disappear with this reaction, have a negative coefficient in (24). Those coefficients and the quantities  $x_1 x_2 \dots y_1 y_2$  etc. define the value of  $\Sigma \varrho (x + y \dots)$ ; if this form is positive, then the temperature decreases; if it is negative, the temperature increases. In some cases this sign is known without further examination. If the new substances occur f. i. only in one or more of the phases, which arise on addition of heat, then, therefore, in  $\Sigma \varrho (x + y \dots)$  only positive terms remain; in accordance with (41) the temperature is lowered, therefore. If the new substances occur only in one of more of the phases, which arise on withdrawal of heat, then in  $\Sigma \varrho (x + y \dots)$  only negative terms remain, consequently the temperature is raised.

Therefore, we reind here the rule, mentioned above sub *b*.

We may still write otherwise (42); with the aid of (34) we are able to express  $n$  of the  $n + 1$  variables  $x_1 x_2$  etc. in one of them; also  $n$  of the  $n + 1$  variables  $y_1 y_2$  in one of those, etc. Instead of (42) we can write, therefore:

$$(\Delta T)_p = - \frac{RT_q}{\Sigma (\varrho \eta)} (\alpha x + \beta y \dots) \dots \dots \dots (43)$$

in which we may give to  $x y$  etc. each index from 1 till  $n + 1$ ;  $\alpha \beta$  etc. have definite positive or negative values, which, however, are dependent on the indices, which we give to  $x y$  etc.

If we add the new substance  $X$  only, then (43) passes into:

$$(\Delta T)_p \cdot (X) = - \frac{RT_q}{\Sigma (\varrho \eta)} \cdot \alpha x \dots \dots \dots (44)$$

In order to indicate that the change in temperature is a result only of the addition of the substance  $X$ , still  $(X)$  is placed behind  $(\Delta T)_p$ . It is apparent from (44) that the sign of  $\alpha$  decides whether the temperature must be raised or lowered.

It is evident now that we may write for (43) also:

$$(\Delta T)_p = (\Delta T)_p(X) + (\Delta T)_p(Y) + \dots \quad (45)$$

This means that the total change in temperature is the algebraic sum of the changes in  $T$ , which each of the new substances would cause, if they were added separately.

Consequently, if each new substance gives by itself an increase (decrease) of  $T$ , then their mixture gives also an increase (decrease) of  $T$ .

If, however, some of the added substances, give an increase of  $T$  and other ones an decrease of  $T$ , then it depends on their mutual ratio, whether their mixture will raise or lower the temperature.

Therefore it must be possible, to add the new substances in such ratio that no change in temperature occurs.

Then must be satisfied:

$$\alpha x + \beta y + \dots = 0 \quad (46)$$

in which, as  $x, y$  etc. are always positive, not all coefficients are able to have the same sign. In general (46) can be satisfied by an infinite number of ways; consequently there is an infinite number of mixtures, which let the temperature unchanged. Of course this is only true at first approximation, for it follows from (40) that  $\Delta T$  is a quantity of the second order.

*(To be continued).*

*Leiden, Lab. of Inorg. Chemistry.*

**Mathematics.** — "On Polar Triangles". By Prof. W. VAN DER WOUDE.  
(Communicated by Prof. J. C. KLUYVER).

(Communicated at the meeting of February 28, 1925).

Dr. G. SCHAAKE has given and investigated a representation of the polar triangles of a conic on the points of a three-dimensional space <sup>1)</sup>. My aim is only to represent the same elements on each other. The result is the same as that of Dr. SCHAAKE. As, however, the method followed by me is very different from that of my predecessor, it seemed allowed to treat the same subject once more.

Besides the conic  $\bar{a}$  a complex of conics  $C$  is assumed relative to which  $\bar{a}$  lies "arbitrarily". Each of these conics has a polar triangle in common with  $\bar{a}$  and generally only one. We can, therefore, consider the 4 homogeneous parameters  $(\kappa, \lambda, \mu, \nu)$  through which a conic  $\bar{c}$  of  $C$  is defined, at the same time as coordinates of that common polar triangle. If then we consider  $(\kappa, \lambda, \mu, \nu)$  as homogeneous coordinates in space, the conics of  $C$  as well as the polar triangles of  $\bar{a}$  are represented on the points of space.

§ 1. Let  $\bar{a}$  be given by the equation:

$$\bar{a} \equiv a_{11} x_1^2 + a_{22} x_2^2 + a_{33} x_3^2 + 2a_{23} x_2 x_3 + 2a_{13} x_1 x_3 + 2a_{12} x_1 x_2 = 0 \quad (1)$$

The equation of the complex  $C$  gets the most simple form if we give the four double lines that are contained in the complex, the equations:

$$x_1 = 0, \quad x_2 = 0, \quad x_3 = 0, \quad x_1 + x_2 + x_3 = 0.$$

In this case  $C$  is represented by:

$$C \equiv \kappa x_1^2 + \lambda x_2^2 + \mu x_3^2 + \nu (x_1 + x_2 + x_3)^2 = 0 \quad \dots \quad (2)$$

If we consider at the same time  $(\kappa, \lambda, \mu, \nu)$  as homogeneous coordinates in space, each set of them, as remarked before, represents a conic  $\bar{c}$  of  $C$  as well as the polar triangle (or triangles) common to  $\bar{a}$  and  $\bar{c}$  on the points of three-dimensional space.

§ 2. In order to find the singular elements of the representation it is necessary to investigate:

<sup>1)</sup> Dr. G. SCHAAKE: Representation of the Polar Triangles of a Conic Section on the Points of Space. These Proceedings, 27, p. 584.

1. the conics  $\bar{c}$  that have more than one polar triangle in common with  $\bar{a}$ .

2. the polar triangles of  $\bar{a}$  that are common to  $\bar{a}$  and more than one conic  $\bar{c}$ .

Both problems are intimately related with that on the double lines of the quadruply infinite linear system of conics  $\Sigma$  defined by  $C$  and  $\bar{a}$ . For this reason we begin by investigating the locus of these double lines.

The system  $\Sigma$  is defined by:

$$\Sigma \equiv C + \varrho \bar{a} \equiv \kappa x_1^2 + \lambda x_2^2 + \mu x_3^2 + \nu (x_1 + x_2 + x_3)^2 + \varrho (a_{11} x_1^2 + a_{22} x_2^2 + a_{33} x_3^2 + 2a_{23} x_2 x_3 + 2a_{13} x_1 x_3 + 2a_{12} x_1 x_2) = 0 \quad (3)$$

If a double line

$$(\xi_1 x_1 + \xi_2 x_2 + \xi_3 x_3)^2 = 0$$

belongs to  $\Sigma$ , it must be possible to determine  $\kappa, \lambda, \mu, \nu, \varrho$  and  $\sigma$  so that

$$\left. \begin{aligned} \sigma \xi_1^2 &= \kappa + \nu + \varrho a_{11} \\ \sigma \xi_2^2 &= \lambda + \nu + \varrho a_{22} \\ \sigma \xi_3^2 &= \mu + \nu + \varrho a_{33} \end{aligned} \right\} \begin{aligned} \sigma \xi_2 \xi_3 &= \nu + \varrho a_{23} \\ \sigma \xi_1 \xi_3 &= \nu + \varrho a_{13} \\ \sigma \xi_1 \xi_2 &= \nu + \varrho a_{12} \end{aligned} \quad (4)$$

For this it is necessary and sufficient that between  $\xi_1, \xi_2, \xi_3$  there exists the relation

$$\Delta \equiv \begin{vmatrix} 1 & a_{23} & \xi_2 \xi_3 \\ 1 & a_{13} & \xi_1 \xi_3 \\ 1 & a_{12} & \xi_1 \xi_2 \end{vmatrix} = 0 \quad (5)$$

As appears from the fact of a simultaneous invariant becoming zero, this is the tangential equation of the conic harmonically inscribed in all the conics of  $\Sigma$ ; the poles of their tangents form a conic  $\delta$ , the reciprocal polar curve of  $\Delta$  relative to  $\bar{a}$ . In other terms:

*The double lines of  $\Sigma$  envelop a conic  $\Delta$ ; we may arrange them in an involution of the third order of which each triple forms the sides of a polar triangle of  $\bar{a}$ .*

§ 3. If a conic  $\bar{c}$  is to have more than one polar triangle in common with  $\bar{a}$ , it must touch  $\bar{a}$  twice and, therefore, define with  $\bar{a}$  a pencil which contains a double line; this double line belongs to  $\Sigma$ . Inversely: each double line of  $\Sigma$  defines a conic  $\bar{c}$  of  $C$  which touches  $\bar{a}$  twice.

We try to find the relations that must exist between  $\kappa, \lambda, \mu, \nu, \varrho$  if this double contact is to take place. They are found by eliminating  $\xi_1, \xi_2, \xi_3$  out of (4) and they are:

$$\left. \begin{aligned} (\kappa + \nu + \varrho a_{11})(\nu + \varrho a_{23}) - (\nu + \varrho a_{12})(\nu + \varrho a_{13}) &= 0 \\ (\lambda + \nu + \varrho a_{22})(\nu + \varrho a_{13}) - (\nu + \varrho a_{12})(\nu + \varrho a_{23}) &= 0 \\ (\mu + \nu + \varrho a_{33})(\nu + \varrho a_{12}) - (\nu + \varrho a_{13})(\nu + \varrho a_{23}) &= 0 \end{aligned} \right\} \dots \dots (6)$$

In this way  $\frac{\kappa}{\varrho}, \frac{\lambda}{\varrho}, \frac{\mu}{\varrho}$  are expressed rationally in  $\frac{\nu}{\varrho}$ ; if we put

$$\frac{\nu}{\varrho} = t,$$

we have e.g.

$$\frac{\kappa}{\varrho} = - (a_{11} + t) + \frac{(a_{12} + t)(a_{13} + t)}{a_{23} + t}.$$

If we consider  $\kappa, \lambda, \mu, \nu$  as homogeneous coordinates in space, (6) represents a rational twisted curve of the fourth order.

*The singular points in space form a rational twisted curve  $r^4$  of the fourth order circumscribed about the coordinate-tetrahedron of which each point corresponds to a conic  $c$  touching  $\bar{a}$  twice and also to an infinite number of polar triangles that are common to  $\bar{a}$  and  $\bar{c}$ . The common side of these triangles touches  $\Delta$ ; the common angular point lies on  $\delta$ . Only one of these triangles is circumscribed about  $\Delta$  and inscribed in  $\delta$ ; each of the sides of this triangle is a double line of  $\Sigma$  (§ 2).*

§ 4. If a polar triangle is common to  $\bar{a}$  and more than one conic, hence at least to a pencil of  $C$ ,  $\Sigma$  must belong to a net which contains  $\bar{a}$ , and which has this triangle as polar triangle. Accordingly the three sides are double lines of  $\Sigma$ ; they form one of the involutorial triangles that are circumscribed about  $\Delta$  and are polar triangles of  $\bar{a}$ . Inversely we found already that each double line of  $\Sigma$  defines only one involutorial triangle.

Consequently to each involutorial triangle there corresponds a net of  $\Sigma$ , hence a pencil of  $C$ , of which it is the common polar triangle; to each involutorial triangle there corresponds, therefore, a pencil of conics, hence a straight line in three-dimensional space.

Three conics  $\bar{c}$ , however, belong to this pencil each of which touches  $\bar{a}$  in the two points of intersection with the sides of the involutorial triangle and corresponds accordingly to a point of  $r^4$ . Hence we have found:

*The singular elements of the plane consist of the involutorial triangles, i.e. the polar triangles of  $\bar{a}$  that are circumscribed about  $\Delta$  and inscribed in  $\delta$ . To each of these triangles there corresponds a pencil of conics and in space a trisecant of  $r^4$ .*

In this way we have found the singular elements; a further discussion of the representation was not our aim. For this we refer to the detailed paper of Dr. SCHAAKE.

**Astronomy.** — "*The proper motion of the globular cluster Messier 13 and its internal motion.*" By ADRIAAN VAN MAANEN.

(Communicated at the meeting of January 31, 1925).

The unexpected discovery of internal motions in the spiral nebulae, from the study of photographs with a relatively short interval made it seem desirable to try analogous measures for one or more globular clusters.

Several photographs of globular clusters were obtained soon after the 80-foot focus arrangement of the 60-inch Mount Wilson reflector had been made available for direct photography (1913). After an interval of over ten years I have measured some plates of the great cluster in Hercules Messier 13, two pair of plates of good quality and with an interval of 9 and 11 years, respectively, being chosen for measurement, which was done with the stereocomparator, with the plates in four positions, East, West, North, and South, respectively, in the direction of the increasing readings of the micrometer screw.

Dr. SHAPLEY had indicated which stars might be members of the cluster and which not, the latter to be used for comparison purposes. With his help fifty comparison stars were selected while sixty-two other stars were measured, which, with considerable probability, might be accepted as members of the cluster. His selection was based on the distance from the center, the magnitude, and the color-index of the individual stars.

As the detailed measures will be published in *Contributions of the Mount Wilson Observatory* N<sup>o</sup>. 284, I shall here give only the results.

That the motions of the members of the cluster are small was at once evidenced by the fact that the annual motions, regardless of the algebraic sign, are only 0".003 in both right ascension and declination, while the analogous values for the comparison stars are 0".006 and 0".010 respectively.

Taking account of the algebraic sign of the motions, we derive for the motion of the cluster with respect to the mean motion of the comparison stars:

$$\mu_{\alpha} = -0''.001 \pm 0''.0004$$

$$\mu_{\delta} = -0''.001 \pm 0''.0003.$$

Subtracting these quantities from  $\mu_{\alpha}$  and  $\mu_{\delta}$  of the individual members of the group, we derive values which represent the internal motions in the cluster. As we might *a priori* expect a contraction or a dispersion, the first thing to do was to derive the mean radial component of the motion. The result is, however, that this component is  $0''.0000 \pm 0''.0003$ ;

there is little reason to anticipate a component at right angles to the radius, except that in the measures of the spiral nebulae such a component has been shown to exist. In Messier 13 this component is  $0''.0005 \pm 0''.0004$  in the direction N W S E. We may thus conclude that the internal motions in the cluster are of the order of  $0''.001$  or less.

Similar result can be derived in the following way: the probable error of the motion in each coordinate as derived from a comparison of the measures of each pair of plates is  $0''.0023$ . If we accept all the 62 stars as real members of the group and that therefore, except for any possible internal motions, they all must have the same motion, we can derive a probable error from the deviations from this mean motion of the group: the result is  $0''.0026$ . It is true that this is slightly larger than the value  $0''.0023$  found before, but it is a well known fact that the internal probable error is always somewhat, and sometimes considerably smaller than the external probable error. The difference between the two values given indicates that the internal motions of the members of the group can scarcely exceed  $0''.001$  in each coordinate.

The results of the measures are thus negative: the motions are too small to be detected in an interval of ten years; they are, nevertheless, of importance for two reasons: firstly, they show that the parallax of  $0''.00009$ , derived by SHAPLEY for Messier 13, cannot be very much too small, as otherwise with the considerable radial velocities found for the globular clusters, we might have expected a measurable motion at right angles to the line of sight; and secondly, the results are of importance in connection with the internal motions found in several spiral nebulae. The plates were taken and measured with the same instruments as in the case of the nebulae and the possibility that their internal motions, which were found to be of the order of  $0''.020$  annually, are due either to the 60-inch reflector or to the stereocomparator, is therefore eliminated. The only possibility that the displacements found in the spirals are not real motions would seem to lie in a systematic difference along the arms of the spirals between the old and the new plates. This possibility is extremely doubtful, because in that case the total displacements would hardly be proportional to the time interval, as was found in several of the spirals for which pairs of plates with different time intervals were available. Moreover, such displacements should be quite different in spirals with a large amount of nebulosity present and in objects where the nebula is practically resolved into individual starlike points. Finally, if the displacements were due to some photographic effect, we should expect such a systematic error to be larger near the centre than near the edge of the spiral, while the measures show just the reverse in all cases.

**Mathematics.** — "*Representation of the Pairs of Points Conjugated relative to a Conic, on the Points of Space.*" By G. SCHAAKE.  
(Communicated by Prof. JAN DE VRIES.)

(Communicated at the meeting of January 31, 1925.)

§ 1. Let a conic  $k^2$  in a plane  $a$  be the projection on  $a$  of a twisted cubic  $k^3$  out of a point  $A$  of the latter cubic. If we associate to each point  $P$  of  $k^3$  its projection  $Q$  on  $a$ , there arises a one-one correspondence  $(P, Q)$  between the points  $P$  of  $k^3$  and the points  $Q$  of  $k^2$  where the point of intersection  $B$  on  $k^2$  of the tangent  $a$  at  $A$  to  $k^3$  with  $a$  corresponds to the point  $A$  of  $k^3$ .

Let  $C_1$  and  $C_2$  be two points of  $a$  associated to each other relative to  $k^2$ . The lines  $BC_1$  and  $BC_2$  cut  $k^2$  outside  $B$  resp. in  $K_1$  and  $K_2$ . The tangents  $t_1$  and  $t_2$  which may be drawn to  $k^2$  resp. at  $K_1$  and  $K_2$ , have their point of intersection  $C$  on the line  $l$  joining  $C_1$  and  $C_2$ . For the pairs  $(K_1, K_2)$  which may be derived from the pairs  $(C_1, C_2)$  of the involution defined on  $l$  by  $k^2$ , form an involution on  $k^2$  the double points of which lie in the points of intersection  $Q_1$  and  $Q_2$  of  $l$  with  $k^2$  and which, therefore, has  $l$  as axis.

The plane  $(A, l)$  contains one chord  $k$  of  $k^3$  which does not pass through  $A$ , the line joining the points  $P_1$  and  $P_2$  of the twisted cubic that correspond to  $Q_1$  and  $Q_2$ . We consider the point of intersection  $S$  of the lines  $AC$  and  $k$  as the image of the pair of points  $(C_1, C_2)$ .

Inversely a pair of points  $C_1$  and  $C_2$  that are associated relative to  $k^2$ , may be derived from any point  $S$ . With a view to this we draw the chord  $k$  of  $k^3$  through  $S$ . We project  $k$  and  $S$  on  $a$  out of  $A$  and find the line  $l$  and the point  $C$  on  $l$ . We determine the points of contact  $K_1$  and  $K_2$  of the tangents  $t_1$  and  $t_2$  to  $k^2$  through  $C$ .  $C_1$  and  $C_2$  are resp. the points of intersection of  $BK_1$  and  $BK_2$  with  $l$ .

In this way we have found a representation of the pairs of points  $C_1$  and  $C_2$  associated to each other relative to  $k^2$ , on the points  $S$  of space.

§ 2. In order to arrive at another way to produce our representation, we examine what corresponds to the system  $S_1$  of the  $\infty^1$  pairs of points associated relative to  $k^2$ , for which  $C_1$  is a fixed point of  $a$ . In this case  $K_1$ , the point of intersection of  $BC_1$  and  $k^2$ , is the same point of this conic for all the individuals of  $S_1$  and  $t_1$  is a fixed tangent of  $k^2$ . The point  $S$  always lies in the tangent plane  $\tau_1$  through  $t_1$  to the cone  $\varkappa$  which projects  $k^3$  out of  $A$ . The chords  $k$  which contain the image points  $S$  of the pairs of points of  $S_1$ , from the scroll  $\varrho$  of the chords

of  $k^3$  which cut the straight line  $AC_1$ , as the projections of these chords on  $\alpha$ , i.e. the lines  $l$  of  $S_1$ , all pass through  $C_1$ . The generatrix of  $\varrho$  through  $A$  lies in the plane  $ABC_1$  through  $AC_1$  and the tangent  $a$ , joins  $A$  to the point of intersection of that plane and  $k^3$ , and is accordingly the line  $AK_1$  in  $\tau_1$ .

The locus of the points of intersection of the lines of  $\varrho$  with  $\tau_1$  is consequently a line  $s_1$  of the scroll  $\sigma$  associated to  $\varrho$ , which passes through the point of intersection  $L_1$  outside  $A$  of  $AK_1$  with  $k^3$ , as the quadratic surface  $\varphi^2$  that contains  $\varrho$  and  $\sigma$ , touches the plane  $\tau_1$  at  $L_1$ . For the tangent plane to  $\varphi^2$  at  $L_1$  is completely defined by the tangent to  $k^3$  and  $AK_1$ .

*The system of the  $\infty^1$  pairs of points conjugated relative to  $k^2$  of which one point is given, is accordingly represented on a line  $s_1$  which touches the cone  $\kappa$  on  $k^3$ .*

§ 3. The straight line  $s_1$  corresponding to a given point  $C_1$  of  $\alpha$  according to § 2, may be found in the following way. We consider the scroll  $\varrho$  of the chords of  $k^3$  which cut the line  $AC_1$ . The generatrices of the corresponding scroll  $\sigma$  which meet  $k^3$  once, all cut the generatrix  $AK_1$  of  $\varrho$  through  $A$  which passes through the point of intersection  $K_1$  outside  $B$  of  $BC_1$  with  $k^2$ , and are, therefore, projected on  $\alpha$  as straight lines through  $K_1$ . Among the lines through  $K_2$  there is one,  $t_1$ , which touches  $k^2$ , so that  $\sigma$  contains one line  $s_1$  which touches  $\kappa$  on  $k^3$ , and that in the point of intersection  $L_1$  outside  $A$  of  $AK_1$  and  $k^3$ . This line is the line  $s_1$  corresponding to  $C_1$ .

The point  $C_1$  of  $\alpha$  which corresponds to a line  $s_1$  which touches  $\kappa$  on  $k^3$ , is found in the following way. We form the scroll  $\varrho$  of the chords  $k$  of  $k^3$  which cut  $s_1$ . The generatrix through  $A$  of the scroll  $\sigma$  associated to  $\varrho$ , cuts  $\alpha$  in  $C_1$ .

The lines  $s$  which are represented in this way on the points of  $\alpha$ , form a congruence  $\Sigma(2, 3)$ . For the lines  $s$  through a point  $S$  of space have their points of contact in the two points of intersection outside  $A$  of the polar plane of  $S$  relative to  $\kappa$  with  $k^3$ , and the lines  $s$  lying in a given plane  $\varphi$  are the tangents that may be drawn in the points of intersection of  $\varphi$  with  $k^3$  to the conic along which  $\varphi$  cuts the cone  $\kappa$ .

*Consequently the pair of points  $(C_1, C_2)$  corresponding in the representation of § 1 to a given point  $S$  of space, is formed by the two points  $C_1$  and  $C_2$  that are associated to the lines  $s_1$  and  $s_2$  through  $S$  of  $\Sigma$ . Inversely the image  $S$  of a pair of points  $(C_1, C_2)$  associated relative to  $k^2$ , is the point of intersection of the lines  $s_1$  and  $s_2$  corresponding to  $C_1$  and  $C_2$ .*

§ 4. If we choose  $S$  on the cone  $\kappa$ ,  $s_1$  and  $s_2$  coincide in the generatrix  $AS$  of  $\kappa$  through  $S$  which cuts  $k^3$  besides in  $A$  in  $L$ , where  $L_1$  and  $L_2$ , the points in which  $s_1$  and  $s_2$  touch the cone  $\kappa$  on  $k^3$ , coincide.

The scroll  $\varrho$  and the associated scroll  $\sigma$  are both formed by the generatrices of  $\varkappa$ . The generatrix of  $\sigma$  passing through the point  $A$  of  $k^3$ , is the tangent  $a$  to  $k^3$  at  $A$  which cuts  $a$  in  $B$ . Hence  $C_1$  and  $C_2$  coincide in  $B$  for any point  $S$  of  $\varkappa$ .

Inversely it appears that an infinite number of lines  $s$  correspond to  $B$ , the generatrices of  $k$ .

*Accordingly the representation has one cardinal pair of points, the pair for which  $C_1$  and  $C_2$  coincide in  $B$ . To this pair there correspond the points of the quadratic cone  $\varkappa$ .*

If we choose for carrier of this pair of points a definite straight line through  $B$  which cuts  $k^2$  besides in  $K$ , according to the construction of § 1 there are only  $\infty^1$  image points, which form the generatrix  $AK$  of  $\varkappa$ .

Through making use of the way of producing our representation indicated in § 1, we should perhaps think that the pairs of points  $(C_1, C_2)$  for which  $C_1$  lies in  $B$ , hence  $C_2$  on the tangent  $b$  at  $B$  to  $k^2$ , are singular. Indeed, for such a pair of points  $K_1$  may be chosen at random on  $k^2$  and  $K_2$  lies in  $B$ . There are an infinite number of points  $C$ , the points of  $b$ . The chord  $k$  becomes the tangent  $a$  to  $k^3$  at  $A$ . If we choose  $C$  in  $B$ ,  $AC$  lies along  $a$  and we find that any point of  $a$  may be considered as the image point of  $(C_1, C_2)$ .

That this is not right, however, appears if we use the way of producing our representation indicated in § 3. The line  $s_1$  corresponding to the point  $C_1$  lying in  $B$ , may be chosen along an arbitrary generatrix of  $\varkappa$ . The line  $AC_2$  belongs to the plane pencil that has  $A$  as vertex and of which the plane is the tangent plane to  $\varkappa$  along  $AB$ , i. e. the plane of osculation of  $k^3$  at  $A$ . The generatrices of this pencil are straight lines of  $\Sigma(2,3)$ . Hence  $AC_2$  is just the line of the scroll  $\sigma$  that may be derived from  $C_2$  which belongs to  $\Sigma$ , that is the line  $s_2$  corresponding to  $C_2$ . This line cuts  $\varkappa$  only in  $A$ , which point is, therefore, the only image point of all the pairs  $(C_1, C_2)$  that are associated relative to  $k^2$  of which one point lies in  $B$ .

Hence  $A$  is a singular point for our representation.  $A$  has this property in common with all the points of  $k^3$ . For if we choose  $S$  on  $k^3$  we have, instead of two lines  $s_1$  and  $s_2$ , a plane pencil of lines  $s$  which has  $S$  for vertex and which lies in the tangent plane  $\tau$  to  $\varkappa$  at  $S$ . The generatrices through  $A$  of the scrolls  $\sigma$  corresponding to these lines  $s$ , form the plane pencil that has  $A$  for vertex and that lies in the plane  $ABS$  which cuts  $a$  along the line  $BK$ , if  $K$  is the projection of  $S$  on  $a$  lying on  $k^2$ . For  $AK$  is always the generatrix through  $A$  of the scrolls  $\varrho$ , and accordingly the projections of all the generatrices of the scrolls  $\sigma$  pass through  $K$ . But the projections of the generatrices through  $A$  of the latter scrolls also pass through  $B$  because the projecting planes pass through  $a$ . Hence the point  $S$  must be considered as the image point of all the pairs of  $BK$  that are associated relative to  $k^2$ .

*Consequently the points of  $k^3$  are singular for our representation. To*

a point  $S$  of  $k^3$  there correspond the pairs of points of the line  $BK$  through  $B$  that are associated relative to  $k^2$ . The pairs of points of which the image lies on  $k^3$ , are the  $\infty^2$  of which the carriers pass through  $B$ .

If we choose  $S$  in  $A$ , there is, besides a plane pencil of lines  $s$ , a cone of similar lines,  $\varkappa$ . Hence the pairs of points  $(C_1, C_2)$  of the line  $b$  are associated to  $A$ , a result already found, on the understanding, however, that the carrier of the coincidence in  $B$  may be chosen arbitrarily through that point.

The latter is also true for any point  $S$  of  $k^3$  relative to the coincidence in  $K$ . This is, for instance, easily seen by the aid of the construction of § 1. If we choose an arbitrary line through  $K$  as carrier, the corresponding line  $k$  is a chord of  $k^3$  through  $S$ . The points  $K_1, K_2$  and  $C$  all coincide in  $K$ . The image point of the chosen coincidence, i.e. the intersection of  $k$  and  $AC$ , in fact always lies in  $S$ .

*The curve  $k^3$  is, therefore, in particular the locus of the image points of the coincidences among the pairs of points that are associated relative to  $k^2$ .*

§ 5. The most simple systems of  $\infty^1$  pairs of points  $(C_1, C_2)$  are the system  $\lambda$  of which all the individuals belong to a given line  $l$  of  $u$ , and the system  $\pi$  of the pairs of which one point is a given point  $P$  of  $u$  and the other point may be chosen at random in the polar line  $p$  of  $P$  relative to  $k^2$ .

To all the individuals of a system  $\lambda$  there corresponds the same chord  $k$  of  $k^3$ , the chord of this curve that does not pass through  $A$  of which the projection on  $u$  coincides with  $l$ . This chord contains the image points of all the pairs of points of  $\lambda$ .

*The system  $\lambda$  of the  $\infty^1$  pairs of points of a line  $l$  that are associated relative to  $k^2$ , are represented on a chord  $k$  of  $k^3$ .*

The points of intersection of  $k$  and  $k^3$  are the image points of the coincidences of  $\lambda$  that lie in the points of intersection of  $l$  and  $k^2$ .

If, in particular,  $l$  is a tangent to  $k^2$ , the involution defined on  $l$  by  $k^2$  becomes parabolic and  $\lambda$  contains only one coincidence. In this case  $\lambda$  is represented on a tangent to  $k^3$ .

In § 2 we found:

*A system  $\pi$  is represented on a straight line  $s$  that touches  $\varkappa$  on  $k^3$ .*

The intersection of  $s$  and  $k^3$  is the image point of the pair of points of  $\pi$  of which the carrier passes through  $B$ . The two points of intersection outside  $k^3$  of  $s$  and the biquadratic surface of the tangents of this curve are the images of the individuals of  $\pi$  for which the point on  $p$  lies in one of the points of intersection of  $p$  and  $k^2$ .

If  $P$  is a point of  $k^2$ , the system  $\pi$  is at the same time a system  $\lambda$ , (save the indefiniteness of the carrier of the coincidence in the point of contact), and is represented on a tangent to  $k^3$ .

§ 6. Of the systems of  $\infty^2$  pairs of points associated relative to  $k^2$ , we shall first treat the system  $II$  of the pairs  $(C_1, C_2)$  of which the carriers

pass through a given point  $P$  of  $\alpha$ . The straight lines  $k$  of these pairs form the scroll of the chords of  $k^3$  that cut  $AP$ .

*The system  $\Pi$  of the  $\infty^2$  pairs of points the carriers of which pass through a given point  $P$ , i. e. a projective inversion with center  $P$  and base  $k^2$ , is accordingly represented on a quadratic surface  $\Phi$  through  $k^3$ .*

Inversely a quadratic surface through  $k^3$  is the image of a similar system, that for which  $P$  lies in the point of intersection with  $\alpha$  of the line through  $A$  of this surface that cuts  $k^3$  only in  $A$ .

If  $P$  lies on  $k^2$ , the image of  $\Pi$  is the cone which projects  $k^3$  out of the point of intersection outside  $A$  of  $AP$  and  $k^3$ .

Two systems  $\Pi$  and  $\Pi'$  corresponding resp. to the points  $P$  and  $P'$ , are represented on two quadratic surfaces  $\Phi$  and  $\Phi'$  which, besides  $k^3$ , have a chord of this curve in common; it is the image of the system of pairs  $(C_1, C_2)$  of the line  $PP'$ .  $\Phi$  and  $\Phi'$  define a pencil of which each surface is the representation of the system of pairs associated relative to  $k^2$  of which the carriers pass through a given point of  $PP'$ .

Let us further investigate the representation of the system  $\mathcal{A}$  of the pairs of which one point lies on a given straight line  $l$ . This system consists of the  $\infty^1$  systems  $\pi$  of the points  $P$  of  $l$  and is, therefore, represented on a surface  $\Psi$  which consists of the  $\infty^1$  corresponding lines  $s$ . As each of the said systems  $\pi$  contains one individual of the system  $\lambda$  of the pairs  $(C_1, C_2)$  of  $l$ ,  $\Psi$  consists of the lines  $s$  that cut the chord  $k$  of  $k^3$  which corresponds to  $l$ .

$\Psi$  has  $k$  as nodal line. The two lines  $s$  through a point  $S$  of  $k$  are the images of the systems  $\pi$  for which  $P$  lies in one of the two points of the pair  $(C_1, C_2)$  that has its image in  $S$ . A plane through  $k$  contains only one generatrix of  $\Psi$ , the line which touches  $\kappa$  in the point of intersection outside  $k$  of this plane and  $k^3$ . As all the generatrices of  $\Psi$  touch the cone  $\kappa$  on  $k^3$ , we find:

*The system  $\mathcal{A}$  of the  $\infty^2$  pairs of points  $(C_1, C_2)$  of which one point lies on a given line  $l$  of  $\alpha$ , is represented on a cubic scroll  $\Psi$  which touches  $\kappa$  on  $k^3$ .*

The single directrix of  $\Psi$  is the line  $s$  which represents the system  $\pi$  that is defined by  $l$  and the pole of  $l$  relative to  $k^2$ .

If  $l$  is a tangent to  $k^2$ ,  $k$  becomes a tangent to  $k^3$  so that this directrix of  $\Psi$  is at the same time a generatrix. In this case  $\Psi$  is a scroll of CAYLEY.

A system  $\Pi$  has  $\infty^1$  pairs of points in common with a system  $\mathcal{A}$ , all the carriers of which pass through  $P$  and which have one point on  $l$ ; the conjugated point always lies on the conic corresponding to  $l$  in the general inversion with center  $P$  and base curve  $k^2$ . This system is represented on the intersection different from  $k^3$  of  $\Phi$  and  $\Psi$ , i. e. a cubic  $(\Phi, \Psi)$  which cuts  $k^3$  in the images of the two coincidences of  $(\Pi, \mathcal{A})$  that lie in the points of intersection of  $l$  and  $k^2$  and in the image point of the pair of points on the line  $BP$ . In the latter image point, the point  $L$  corresponding to  $P$ , the surface  $\Phi$  touches the cone  $\kappa$  according

to § 2; hence this is also the case for the curve  $(\Phi, \Psi)$ . The two former points of  $k^3$  are the intersections of the chord  $k$  corresponding to  $l$  and  $k^3$ . These are cuspidal points of  $\Psi$ ; the two corresponding torsal lines are the tangents to  $k^3$  at these points, the images of the systems  $\pi$  of which the point  $P$  lies in one of the intersections of  $l$  and  $k^2$ . As in these cuspidal points of  $\Psi$   $\Phi$  and  $\Psi$  have only the tangent to  $k^3$  as a common tangent, the curve  $(\Phi, \Psi)$  must touch  $k^3$  at this point.

*A system  $(II, A)$  is accordingly represented on a twisted cubic that touches  $\kappa$  once on  $k^3$  and the latter curve twice.*

If  $l$  is the polar line of  $P$  relative to  $k^2$ ,  $(II, A)$  consists of the two systems  $\lambda$  corresponding to the tangents to  $k^2$  through  $P$ , and of the system  $\pi$  of  $P$ . In this case the image consists of two tangents of  $k^3$ , and the line touching  $\kappa$  on  $k^3$  which cuts the two said tangents.

The system which is common to two systems  $A$  and  $A'$  which correspond to the lines  $l$  and  $l'$ , consists of the system  $\pi$  of the point  $P$  that lies in the intersection of  $l$  and  $l'$ , and of the system  $(A, A')$  of the  $\infty^1$  pairs of points associated relative to  $k^2$  of which one point belongs to  $l$  and the other to  $l'$ . The former system is represented on the line  $s$  belonging to  $\Psi$  and  $\Psi'$  which touches  $\kappa$  on  $k^3$  and cuts  $k$  and  $k'$ . Besides  $s$  and  $k^3$ , along which curve  $\Psi$  and  $\Psi'$  touch each other, these surfaces have a conic  $(\Psi, \Psi')$  in common, the image of  $(A, A')$ . As the carriers of  $(A, A')$  envelop a conic, there are two pairs of points of this system the joins of which pass through  $B$ , so that the conic  $(A, A')$  cuts the curve  $k^3$  in two points, where it touches  $\kappa$ .

*Consequently the system of the  $\infty^1$  pairs of points that have a point on each of two given lines of  $\alpha$ , is represented on a conic which touches  $\kappa$  twice on  $k^3$ .*

A check of the latter two results is given by the fact that the class of the envelope of the carriers and the order of the curve of the points of the individuals of a system of  $\infty^1$  pairs of points  $(C_1, C_2)$  are resp. equal to the numbers of points of intersection outside  $k^3$  of the image curve with a surface  $\Phi$  and with a surface  $\Psi$ .

§ 7. The pairs of points that are associated to each other relative to  $k^2$  as well as relative to another conic  $k'^2$  of  $\alpha$ , form a quadratic involution  $I$ , which is represented on a surface  $X$ . The class of  $I$ , i.e. the number of pairs of  $I$  which belong to a straight line  $l$  of  $\alpha$ , is one. For the points of the pair of  $I$  on  $l$  are the points of intersection of  $l$  with the conic described by  $C_2$  if  $C_1$  moves on  $l$ , or the double points of the involution which is defined by the pairs of points lying on  $k^2$  and  $k'^2$ . As, accordingly, any line through  $B$  contains one pair of points of  $I$ ,  $k^3$  is a single curve of  $X$ . A chord  $k$  of  $k^3$  cuts  $X$  outside this curve in one point, the image of the pair of points of  $I$  which lies on the line  $l$  of  $\alpha$  corresponding to  $k$ . Consequently  $X$  is a cubic surface. As the involution  $I$  contains one pair of points, of which one point is given,

a straight line touching  $\kappa$  on  $k^3$  cuts the surface  $X$  only once outside  $k^3$ . Hence the surface  $X$  must touch  $k^3$  on  $\kappa$ .

The involution  $I$  has four double points, the points of intersection  $Q_1, \dots, Q_4$  of  $k^2$  and  $k'^2$ , which are resp. represented on the corresponding points  $P_1, \dots, P_4$  of  $k^3$ . As no line through a point  $Q_i$  on which there lies no other point  $Q_i$ , contains any pair of  $I$  besides the coincidence in  $Q_i$ , no chord of  $k^3$  through  $P_i$  which does not contain any of the other points  $P$ , has any point in common with  $X$  outside  $P_i$  and  $k^3$ . The points  $P_1, \dots, P_4$  are necessarily conical points of  $X$ . The lines  $Q_i Q_k$  are singular for  $I$ , as all the pairs of points of  $Q_i Q_k$  that are associated relative to  $k^2$ , are also associated relative to  $k'^2$  and belong, accordingly, to  $I$ . The lines  $P_i P_k$  belong, therefore, all to  $X$ .

*Consequently a quadratic involution of pairs of points associated relative to  $k^2$ , is represented on a surface  $X$  that contains four conical points on  $k^3$ .*

Such a surface may be represented on a plane  $\chi$  by means of a cubical involution. Through this representation the six lines  $P_i P_k$  are transformed into the angular points  $R_{ik}$  of a complete quadrilateral. A twisted cubic through the points  $P_i$  is transformed into a straight line of  $\chi$ . The diagonals of the said complete quadrilateral are the images of three lines of  $\chi$  different from  $P_i P_k$  which cut  $k^3$  once, touch the cone  $\kappa$  in the points of intersection with  $k^3$ , and form a triangle. These three lines  $s$  are the images of systems  $\pi$  of  $I$  of which the points  $P$  are singular points of  $I$ , to each of which in  $I$  the whole polar line relative to  $k^2$  is associated. As each pair of these systems  $\pi$  has a pair of points in common, the points  $P$  and the associated straight lines are resp. the angular points and the sides of a polar triangle of  $k^2$ . The straight line of  $X$  that corresponds to the diagonal  $R_{ik} R_{lm}$ , cuts the lines  $P_i P_k$  and  $P_l P_m$  so that the associated system  $\pi$  of  $I$  has its point  $P$  in the intersection of  $Q_i Q_k$  and  $Q_l Q_m$ , as it contains one pair of points of each of these lines. The line associated to this point  $P$  in  $I$ , joins the other two diagonal-points of the complete quadrilateral  $Q_1 Q_2 Q_3 Q_4$ .

A cubic surface through  $k^3$  which touches  $\kappa$  on  $k^3$ , is always the image of such a quadratic involution. For a surface of this kind has one point of intersection with a line  $s$  that is not singular so that to a point of  $\alpha$  one point is associated in the corresponding involution. Further the surface cuts a conic which touches  $\kappa$  twice on  $k^3$ , in two points that are not singular for the representation, so that  $I$  contains two pairs of points that have a point on each of two given lines of  $\alpha$ , and if a point describes a straight line of  $\alpha$  the point associated to it in  $I$  describes a conic.  $I$  cannot be an inversion relative to  $k^2$ , as this is represented on a quadratic surface.

*Accordingly a cubic surface through  $k^3$  which touches a quadratic projecting cone of this curve in each point of  $k^3$ , has always four conical points on  $k^3$ .*

If  $I$  has a coincidence in  $B$ , the quadratic cone  $\varkappa$  splits off from  $X$ . Consequently  $I$  is represented on a plane.

Let us assume besides  $I$  an involution  $I'$  which is defined by  $k^2$  and a third conic  $k'^2$ .  $I'$  is represented on a surface  $X'$ . The surfaces  $X$  and  $X'$  define a pencil of cubic surfaces that touch  $\varkappa$  on  $k^3$ , the image of the pencil of quadratic involutions defined by  $I$  and  $I'$ , of which each individual may be derived from a pencil of conics containing  $k^2$  out of the net defined by  $k^2$ ,  $k'^2$  and  $k'^2$ . The individual of the said pencil of surfaces which passes through a point of  $\varkappa$  outside  $k^3$ , must degenerate into  $\varkappa$  and a plane, as a non-degenerate surface of the pencil cannot have any point in common with  $\varkappa$  outside  $k^3$ , along which curve it touches  $\varkappa$ . The corresponding quadratic involution may be derived from the pencil with a base point in  $B$  of the net defined by  $k^2$ ,  $k'^2$  and  $k'^2$ .

Hence the intersection of  $X$  and  $X'$  consists of  $k^3$ , counted double, and a plane cubic  $(X, X')$  which touches  $\varkappa$  in three points on  $k^3$ . This curve is the image of the system  $(I, I')$  of the pairs of points that are associated relative to  $k^2$ ,  $k'^2$  and  $k'^2$ . As  $(X, X')$  has three points that are not singular for the representation, in common with a surface  $\Phi$  as well as with a surface  $\Psi$ , the locus of the pairs of points of  $(I, I')$  is a cubic, and the carriers of the pairs of  $(I, I')$  envelop a curve of the third class. As  $(X, X')$  has one point in common with each of the lines of the surfaces of the pencil defined by  $X$  and  $X'$  which cut  $k^3$  once, the locus of the pairs of  $(I, I')$  passes through the singular points of the involutions of the pencil defined by  $I$  and  $I'$ . Accordingly this locus is the Jacobian of the net defined by  $k^2$ ,  $k'^2$  and  $k'^2$ .

*The involution of the pairs of points on the Jacobian of a net containing  $k^2$  which are associated relative to all the conics of the net, is represented on a plane cubic which touches  $\varkappa$  three times on  $k^3$ .*

Besides  $k^3$  three surfaces  $X, X'$  and  $X''$  have three points in common on a straight line. This line is the intersection  $g$  of the three planes containing the intersections of each pair of the chosen surfaces. The surfaces  $X, X'$  and  $X''$  define a net; the degenerate individuals consist of the planes through  $g$  and  $\varkappa$ . A plane through  $g$  cuts this net along a pencil of cubics of which three base points lie in the three isolated base points of the net and the remaining six coincide in pairs in the three points of intersection with  $k^3$ . A surface  $\Psi$  through two of the isolated base points must also pass through the third. For  $\Psi$  cuts the plane through  $g$  along a cubic which passes through eight base points of the said pencil that lie independently, and which must, therefore, also contain the ninth base point <sup>1)</sup>.

<sup>1)</sup> The independence appears from the fact that through any seven of the base points we can pass a cubic which does not contain the eighth base point. In the first place we can choose the intersection with  $\varkappa$  and a straight line through an isolated base point of the net, further the conic through the base points and the line which joins two base points lying on  $k^3$ .

Hence the three involutions  $I, I'$  and  $I''$  have three pairs of points in common, so that the line which joins a point of one of these pairs to a point of the second, also contains a point of the third. Consequently the common pairs of points of  $I, I'$  and  $I''$  form the pairs of opposite angular points of a complete quadrilateral. If  $I, I'$  and  $I''$  are defined, besides by  $k^2$ , resp. by  $k'^2, k''^2$  and  $k'''^2$ , these pairs of points are associated relative to all the conics of the linear system defined by  $k^2, \dots, k'''^2$ .

*In this way we have found a proof of the theorem that the pairs of points which are associated relative to all the conics of a complex, are the pairs of opposite angular points of a complete quadrilateral.*

§ 8. A plane  $V$  of points  $S$  is the image of a system of  $\infty^2$  pairs of points  $(C_1, C_2)$ . As  $V$  has resp. one, one and two points in common with a line  $s$ , a chord  $k$  and a conic which touches  $\kappa$  twice on  $k^3$ , we may conclude that to  $V$  there corresponds a quadratic involution of pairs of points associated relative to  $k^2$ . This involution has a coincidence in  $B$ , because  $V$  cuts all the generatrices of  $\kappa$ . It may be derived from a pencil of conics containing  $k^2$  which has a base point in  $B$ .

*A plane is the image of a quadratic involution of pairs of points associated relative to  $k^2$  which has a coincidence in  $B$ .*

The six singular lines of the involution are represented on the points of intersection of  $V$  and  $k^3$  and on the three chords of this curve in  $V$ . The three systems  $\pi$  each of which is defined by a singular point of the involution and the polar line associated to it, correspond to the three lines in  $V$  which touch  $\kappa$  on  $k^3$ . A surface  $\Psi$  cuts  $V$  along a cubic which touches  $\kappa$  in the three points of intersection with  $k^3$ , the image of the correspondence between the points of a straight line and the conic associated to it through the involution, which, as the said cubic cuts any line  $s$  in  $V$  once outside  $k^3$ , passes through the singular points of the involution.

To a plane through  $A$  as well as to an arbitrary tangent plane to  $k^3$  there corresponds an involution with two coinciding coincidences, etc.

As a special case let us choose for  $V$  a tangent plane to  $\kappa$ . We can consider  $V$  as consisting of lines  $s$  which form a plane pencil the vertex of which lies in the point where  $V$  touches the curve  $k^3$ . Accordingly the associated system is formed by the systems  $\pi$  that have their point  $P$  on a straight line of  $\alpha$  through  $B$ ; it is, therefore, a system  $\Lambda$ . A tangent plane to  $\kappa$  forms with  $\kappa$  a degeneration of a surface  $\Psi$ .

*Consequently the system of the pairs of points of which one point lies on a straight line through  $B$ , is represented on a tangent plane to  $\kappa$ .*

In particular the plane of osculation to  $k^3$  at  $A$  is the image of the system of the pairs of which one point lies on the tangent  $b$  to  $k^2$  at  $B$ .

The points  $S$  of a line  $g$  in space are the images of the pairs  $(C_1, C_2)$  of a system  $\gamma$  of  $\infty^1$  pairs of points that are associated relative to  $k^2$ .

As  $g$  cuts a surface  $\Phi$  and a surface  $\Psi$  resp. twice and three times, the carriers of  $\gamma$  envelop a conic and the locus of the pairs of  $\gamma$  is a cubic. This curve has a node in  $B$ . For  $\gamma$  contains two coincidences lying in  $B$ , the carriers of which are the lines through  $B$  which cut the generatrices of  $\kappa$  meeting  $g$ , on  $k^2$ . The system  $\gamma$  consists of the common pairs of points of the pencil of quadratic involutions which is represented on the pencil of planes of which  $g$  is the axis, hence of the pairs of points that are associated relative to all the conics of a net that has a base point in  $B$ . From the curve of the third class which is enveloped by the carriers of a general net, there splits off the plane pencil that has  $B$  for vertex.

*Accordingly a line  $g$  is the image of the involution defined by a net of conics containing  $k^2$  that has its base point in  $B$ , on its Jacobian.*

The lines  $k$  corresponding to the carriers of  $\gamma$ , are the chords of  $k^3$  which cut  $g$ . They form  $\infty^1$  triangles inscribed in  $k^3$ , to which there correspond triangles inscribed in  $k^2$  the sides of which are carriers of  $\gamma$ .

*Consequently the conic enveloped by the carriers of  $\gamma$ , is inscribed in  $k^2$ , hence also in all the conics of the net from which  $\gamma$  is derived.*

The lines  $g$  of a plane  $V$  are the images of systems  $\gamma$  of the quadratic involution  $I$  corresponding to  $V$ . The loci of the pairs of points of these systems  $\gamma$  are cubics which are *invariant* for  $I$ . They have a node in  $B$ , pass through the three singular points of  $I$ , and cut the singular lines of  $I$  which does not pass through  $B$ , in a pair of points that are associated relative to  $k^2$ . There are *four* systems of such cubics that are invariant for  $I$ .

A line  $g$  that cuts  $k^3$  once, has resp. one and two points which are not singular for the representation, in common with a surface  $\Phi$  and a surface  $\Psi$ . Accordingly the locus of the pairs of points of the corresponding system  $\gamma$  is a conic and the carriers of  $\gamma$  form a plane pencil. From the system  $\gamma$  corresponding to an arbitrary line  $g$ , also the involution has split off which is defined through  $k^2$  on a straight line through  $B$ , and the system of pairs of points of which the carriers form the plane pencil that has for vertex the projection of the point of intersection of  $g$  and  $k^3$ .

To a line cutting  $k^3$  once, there correspond, accordingly, a conic and a plane pencil. The conic passes through  $B$ , as  $\gamma$  contains a coincidence in this point, which is represented on the point of intersection outside  $k^3$  of  $g$  and  $\kappa$ . The vertex of the plane pencil is the center of an inversion which is represented on the quadratic surface  $\Phi$  of the chords of  $k^3$  cutting  $g$ , and through which the conic is transformed into itself.

From this it appears that the generatrices of a quadratic surface  $\Phi$  corresponding to a point  $P$  of  $\alpha$  that cut  $k^3$  once, are associated to the conics through  $B$  which are invariant for an inversion with center  $P$  and base curve  $k^2$ .

As  $\gamma$  has two coincidences, one in  $B$  and one in the point of  $k^2$  that corresponds to the point of intersection of  $g$  and  $k^3$  <sup>1)</sup>, we find:

*The Jacobian of a net of conics containing  $k^2$  which has two base points one of which lies in  $B$ , degenerates into the line joining these base points and a conic through the base points. The involution defined on the conic by the net, is represented on a line that cuts  $k^3$  once.*

The three plane pencils in a plane  $V$  of lines which cut  $k^3$  once, give three systems of conics that are invariant for the involution  $I$  corresponding to  $V$ . Such a system consists of the conics passing through  $B$  and another double point of  $I$  as well as through the two singular points which do not lie on the side of the two said double points and which contain a pair of points associated relative to  $k^2$ , on the side through the angular points of which the conics do not pass.

In all, six systems of this kind correspond to  $I$ . The other three are represented on conics which pass through the points of intersection of  $k^3$  and  $V$  and which, besides, touch  $\kappa$  in the point of intersection of  $k^3$  and  $V$  corresponding to the double point of  $I$  through which the conics of such a system do not pass <sup>2)</sup>.

A line  $g$  through  $A$  is the image of the system of the  $\infty^1$  pairs of points associated relative to  $k^2$ , of the two straight lines through  $B, BK_1$  and  $BK_2$ , if  $K_1$  and  $K_2$  are the points of contact of the tangents to  $k^2$  through the point of intersection  $C$  of  $g$  and  $a$ . From the system associated to an arbitrary line  $g$  there splits off besides the parabolic involution which is defined by  $k^2$  on the tangent  $b$  at  $B$ . The corresponding net of conics has two base points which coincide in  $B$ .

*The Jacobian of a net with two base points that coincide in  $B$ , degenerates into the common tangent of the conics of this net and into two straight lines through  $B$ . The system of the pairs of points associated relative to the net of which each of the latter two lines contains one point, is represented on a straight line through  $A$ .*

If  $g$  is a chord  $k$  of  $k^3$ , the corresponding net has three base points one of which lies in  $B$ . The Jacobian degenerates into the line  $l$  of  $a$  which corresponds to  $k$  that joins the base points different from  $B$ , and into the two lines which may be drawn through  $B$  and the other two base points, which lines are associated to the points of intersection of  $k$  and  $k^3$ .

To a straight line  $g$  that touches  $\kappa$  on  $k^3$ , there corresponds a net with two base points for which the Jacobian has degenerated into the join of these base points, counted double, and into the line  $p$  of the system  $\pi$  which is represented on the said straight line. The net associated to a tangent of  $k^3$ , has a base point in  $B$  and two coinciding base points outside  $B$ . The Jacobian degenerates into the common tangent and into the line joining the point of contact and  $B$ , counted double.

<sup>1)</sup> Cf. § 9, par. 2.

<sup>2)</sup> Cf. § 9.

§ 9. A curve  $k^n$  is the image of a system  $\gamma$  of  $\infty^1$  pairs of points that are associated relative to  $k^2$ . We suppose that  $k^n$  touches  $\varkappa p_1$  times on  $k^3$  outside  $A$ , and cuts  $k^3$  besides  $p_2$  times outside  $A$ .

If a system  $\gamma$  has a pair of points on a straight line through  $B$ , the image curve cuts  $k^3$ . If the image  $S$  on the image curve approaches the point of intersection with  $k^3$ , the chord of  $k^3$  through  $S$  approaches the line joining the said point of intersection to  $A$ . In this case the image curve must touch  $\varkappa$  on  $k^3$ . A point where the image curve cuts  $k^3$  but does not touch  $\varkappa$ , is consequently the image of a coincidence of  $\gamma$ , and to a point where the image curve touches  $k^3$ , there corresponds a double coincidence of  $\gamma$ , which, however, only forms a single pair of this system.

The class of the system  $\gamma$  which is represented on  $k^n$ , i. e. the class of the envelope of the carriers of  $\gamma$ , is equal to the number of points of intersection of  $k^n$  and a surface  $\Phi$  that are not singular for the representation, hence:  $2n - p_1 - p_2$ , and the order, i. e. the order of the locus of the pairs of points of  $\gamma$ , is equal to the number of points of intersection of  $k^n$  and a surface  $\Psi$  that are not singular for the representation, hence to  $3n - 2p_1 - p_2$ . As  $k^n$  cuts the cone  $\varkappa$  outside  $k^3$  in  $2n - 2p_1 - p_2$  points,  $\gamma$  has  $2n - 2p_1 - p_2$  coincidences in  $B$ , and accordingly the locus of the pairs of points of  $\gamma$  has a  $2n - 2p_1 - p_2$ -fold point in  $B$ .

*A curve  $k^n$  of the order  $n$  which touches  $\varkappa p_1$  times on  $k^3$  outside  $A$ , and which besides cuts  $k^3 p_1$  times outside  $A$ , is the image of a system  $\gamma$  of  $\infty^1$  pairs of points associated relative to  $k^2$  of the class  $2n - p_1 - p_2$  and of the order  $3n - 2p_1 - p_2$  which has  $2n - 2p_1 - p_2$  coincidences in  $B$ .*

The number of the coincidences of  $\gamma$  outside  $B$  is  $p_2$ .

Let us now investigate the representation of a system  $\gamma$  of  $\infty^1$  pairs of points associated relative to  $k^2$  of the class  $\mu$  and the order  $\nu$  that does not have any coincidence in  $B$  and does not contain either any pair associated relative to  $k^2$  which belongs to the tangent  $b$  at  $B$  to  $k^2$ . The latter two conditions can be satisfied by a system  $\gamma$  of any kind.

As the image curve of  $\gamma$  does not pass through  $A$ , we find by solving  $n$ ,  $p_1$ , and  $p_2$  out of the equations

$$\begin{aligned} 2n - p_1 - p_2 &= \mu \\ 3n - 2p_1 - p_2 &= \nu \\ 2n - 2p_1 - p_2 &= 0 : \end{aligned}$$

*The image of a system  $\gamma$  of  $\infty^1$  pairs of points associated relative to  $k^2$  of the class  $\mu$  and of the order  $\nu$  that does not contain any pair of which one point lies in  $B$ , is a curve of the order  $\nu$  which touches  $\varkappa \mu$  times on  $k^3$  outside  $A$  and which besides cuts  $k^3 2(\nu - \mu)$  times outside  $A$ .*

Hence the order of a system of  $\infty^1$  pairs of points associated relative to  $k^2$ , is always greater than or equal to the class.

Further:

A system of  $\infty^1$  pairs of points associated relative to  $k^2$  of the order  $\nu$  and the class  $\mu$  contains  $2(\nu - \mu)$  coincidences.

A surface  $\Omega$  of the order  $r$  which contains  $s$  leaves through  $k^3$  touching  $\kappa$  on  $k^3$  and of which  $t$  more leaves pass through  $k^3$ , is the image of a system  $I'$  of  $\infty^2$  pairs of points associated relative to  $k^2$ . We suppose that  $A$  as well as any point of  $k^3$  is an  $(s + t)$ -fold point of  $\Omega$ .

The order of  $I'$ , i.e. the number of pairs of this system of which one point lies in a given point of  $a$ , hence the number of points of intersection of  $\Omega$  with a straight line  $s$  which touches  $\kappa$  on  $k^3$ , that are not singular for the representation, is  $r - 2s - t$  and the class, i.e. the number of pairs of  $I'$  that belong to a given straight line of  $a$ , hence the number of non-singular points of intersection of  $\Omega$  and a chord  $k$  of  $k^3$ , is equal to  $r - 2s - 2t$ . As each generatrix of  $\kappa$  cuts the surface  $\Omega$  in  $r - 3s - 2t$  non-singular points,  $I'$  has an  $r - 3s - 2t$ -fold full coincidence in  $B$ , i.e. a coincidence of which the carrier is indefinite and which forms an  $r - 3s - 2t$ -fold pair of points of  $I'$ .

A surface  $\Omega$  of the order  $r$  containing  $s$  leaves through  $k^3$  which touch  $\kappa$  on  $k^3$ , and which has  $t$  more leaves through  $k^3$  and an  $(s + t)$ -fold point in  $A$ , is the image of a system of  $\infty^2$  pairs of points associated relative to  $k^2$  of the order  $r - 2s - t$  and of the class  $r - 2s - 2t$  that has an  $(r - 3s - 2t)$ -fold full coincidence in  $C$ .

The conic  $k^2$  is a  $t$ -fold curve of coincidence for  $I'$ .

The pairs of  $I'$  define an involutorial correspondence  $(r - 2s - t, r - 2s - t)$ . If a point describes a straight line of  $a$ , the points corresponding to it in this involutorial correspondence describe a curve of which the order is equal to the number of non-singular points of intersection of  $\Omega$  with the image of the system of the  $\infty^1$  pairs of points associated relative to  $k^2$  which have a point on each of two given straight lines of  $a$ , i.e. according to § 6 or according to the second theorem of this § a conic which touches  $\kappa$  twice on  $k^3$ . For the order of the curve associated to a straight line, we find therefore  $2r - 4s - 2t$ .

Inversely we investigate the representation of a system  $I'$  of the order  $\varrho$  and of the class  $\sigma$  that has no full coincidence in  $B$ . The latter condition may again be satisfied by a system  $I'$  of any kind. A straight line of  $a$  through  $B$  contains as many pairs of points non-singular for the representation and different from the coincidence in  $B$ , as an arbitrary line of  $a$ . A chord of  $k^3$  through  $A$  must cut  $\Omega$  outside  $A$  in as many points as a chord through an arbitrary point  $P$  of  $k^3$  has in common with  $\Omega$  outside  $P$ , so that  $A$  and  $P$  are points of the same multiplicity for  $\Omega$ .

We may, therefore, find the characteristic numbers  $r$ ,  $s$  and  $t$  of  $\Omega$  by solving them out of the equations:

$$\begin{aligned} r - 2s - t &= \varrho \\ r - 2s - 2t &= \sigma \\ r - 3s - 2t &= \sigma. \end{aligned}$$

We find:

A system  $I'$  of the order  $\varrho$  and of the class  $\sigma$  that has no full coincidence in  $B$ , is represented on a surface  $\Omega$  of the order  $2\varrho + \sigma$  which contains  $\sigma$  leaves through  $k^3$  touching  $\kappa$  on  $k^3$ , which has, besides,  $\varrho - \sigma$  leaves through  $k^3$ , and which contains a  $\varrho$ -fold point in  $A$ .

Accordingly the order of a system  $I'$  is always greater than the class.

For a system of  $\infty^2$  pairs of points associated relative to  $k^2$  of the order  $\varrho$  and of the class  $\sigma$ ,  $k^2$  is a  $(\varrho - \sigma)$ -fold curve of coincidence. For  $2\varrho - \varrho - \sigma = \varrho - \sigma$  of the points of intersection outside  $k^3$  of an arbitrary straight line  $s$  touching  $\kappa$  on  $k^3$  lie on  $k^3$  if we choose for  $s$  a tangent to this curve.

The order of the curve which in the involution defined by  $I'$  is associated to a straight line, is equal to the number of non-singular points of intersection of  $\Omega$  and a conic which touches  $\kappa$  twice on  $k^3$ ; hence it is equal to  $2\varrho$ .

§ 10. A system  $\gamma$  of  $\infty^1$  and a system  $I'$  of  $\infty^2$  pairs of points associated relative to  $k^2$ , have as many pairs in common as the image curve of  $\gamma$  and the image surface of  $I'$  have points of intersection that are not singular for the representation. If the class and the order of  $\gamma$  are resp.  $\mu$  and  $\nu$ , the class and the order of  $I'$  resp.  $\varrho$  and  $\sigma$ , we find for the number of the points of intersection in question:

$$\nu(2\varrho + \sigma) - \mu(2\sigma + \varrho - \sigma) - 2(\nu - \mu)\varrho = \mu\varrho - \mu\sigma + \nu\sigma.$$

A system of  $\infty^1$  pairs of points associated relative to  $k^2$  of the class  $\mu$  and the order  $\nu$  has

$$\mu(\varrho - \sigma) + \nu\sigma$$

pairs in common with a system of  $\infty^2$  similar pairs of the order  $\varrho$  and the class  $\sigma$ .

The intersection  $(\Omega, \Omega')$  different from  $k^3$  of the surfaces  $\Omega$  and  $\Omega'$  which represent two systems  $I'(\varrho, \sigma)$  and  $I''(\varrho', \sigma')$ , is of the order:

$$(2\varrho + \sigma)(2\varrho' + \sigma') - 3\varrho\varrho' - 3\sigma\sigma' = \varrho\varrho' + 2\varrho\sigma' + 2\sigma\varrho' - 2\sigma\sigma'.$$

The curve which  $\Omega$  has in common with a surface  $\Phi$ , cuts each chord of  $k^3$  on this surface in  $\sigma$  points, each straight line of  $\Phi$  cutting  $k^3$  once, in  $\varrho + \sigma$  points, and it is accordingly a curve  $(\sigma, \varrho + \sigma)$  of this quadratic surface. According to a well known theorem this curve has

$$\sigma(\varrho' + \sigma') + \sigma'(\varrho + \sigma) = \varrho\sigma' + \sigma\varrho' + 2\sigma\sigma'$$

points in common with the curve  $(\sigma', \varrho + \sigma')$  along which  $\Omega'$  cuts  $\Phi$  outside  $k^3$ .

According to § 2  $\Phi$  touches the cone  $\kappa$  in one point of  $k^3$ , hence also  $\sigma$  leaves of  $\Omega$  and  $\sigma'$  leaves of  $\Omega'$ . The curves of intersection different from  $k^3$  of  $\Omega$  and  $\Phi$  and of  $\Omega'$  and  $\Phi$  have resp. a  $\sigma$ - and a  $\sigma'$ -fold

point in this point of  $k^3$ ; they cut each other, therefore, outside  $k^3$  in  $\varrho\sigma' + \sigma\varrho' + \sigma\sigma'$

points.

These are the points of intersection outside  $k^3$  of the curve  $(\Omega, \Omega')$  and  $\psi$ . Hence in all  $(\Omega, \Omega')$  cuts the curve  $k^3$  in

$$2(\varrho\varrho' + 2\varrho\sigma' + 2\sigma\varrho' - 2\sigma\sigma') - \varrho\sigma' - \sigma\varrho' - \sigma\sigma' = 2\varrho\varrho' + 3\varrho\sigma' + 3\sigma\varrho' - 5\sigma\sigma'$$

points.

If we choose  $I'$  and  $I''$  so that the system common to these systems does not contain any pair of which one point lies in  $B$ , the curve  $(\Omega, \Omega')$  does not pass through  $A$ , nor does it cut the cone  $\kappa$  outside  $k^3$ . The points of intersection outside  $k^3$  of  $(\Omega, \Omega')$  and an arbitrary quadratic surface through  $k^3$ , must lie on  $k^3$  if we choose the cone  $\kappa$  for this surface.

Consequently  $(\Omega, \Omega')$  touches the cone  $\kappa$  in  $\varrho\sigma' + \sigma\varrho' + \sigma\sigma'$  points on  $k^3$ , and cuts this curve besides in  $2\varrho\varrho' + 2\varrho\sigma' + 2\sigma\varrho' - 6\sigma\sigma'$  points.

We find therefore by the aid of the first theorem of § 9:

*Two systems  $I'(\varrho, \sigma)$  and  $I''(\varrho', \sigma')$  have in common a system of  $\infty^1$  pairs of points associated relative to  $k^2$  of the class  $\varrho\sigma' + \sigma\varrho' + \sigma\sigma'$  and of the order  $\varrho\varrho' + 2\varrho\sigma' + 2\sigma\varrho' - 2\sigma\sigma'$ .*

If we determine the number of non-singular points of intersection of  $(\Omega, \Omega')$  with the image surface of a third system  $I'''(\varrho'', \sigma'')$ , we find:

*Three systems  $I'(\varrho, \sigma)$ ,  $I''(\varrho', \sigma')$  and  $I'''(\varrho'', \sigma'')$  have*

$$\varrho\varrho'\sigma'' + \varrho\sigma'\varrho'' + \varrho\sigma'\sigma'' + \sigma\varrho'\varrho'' + \sigma\varrho'\sigma'' + \sigma\sigma'\varrho'' - 3\sigma\sigma'\sigma''$$

*pairs of points in common.*

**Mathematics.** — "On Derived Functions of a Real Variable." By Prof. J. WOLFF. (Communicated by Prof. R. WEITZENBÖCK.)

(Communicated at the meeting of February 28, 1925.)

1. In the Proc. of the London Math. Society, serie 2, vol. 9, 1911, p. 360—368, W. H. YOUNG gives a number of sufficient conditions under which the product of a derived function  $f'$  and a function  $\Phi$  is again a derived function.

In this paper we give a few extensions of YOUNG's theorems and we show by an example that we cannot expect any progress worth mentioning in this train of thought (theorem C).

2. We shall prove the following theorems:

A. *If  $f'$  is summable and if  $\Phi$  has finite derived numbers,  $f'\Phi$  is a derivative.*

This theorem is an extension of the following theorem of YOUNG: "if  $f'$  is the derivative of a function of limited variation and  $\Phi$  has a finite summable derivative,  $f'\Phi$  is a derivative."

B. *If  $f'$  is limited,  $\Phi$  approximately continuous and limited,  $f'\Phi$  is a derivative."*

This is an extension of YOUNG's theorem:

"If  $f'$  is limited and  $\Phi$  is continuous,  $f'\Phi$  is a derivative".

C. *There are summable derivatives  $f'$  with only one point of discontinuity, and continuous functions  $\Phi$  so that  $f'\Phi$  is no derivative.*

3. In order to prove A and B we remark that in both cases  $f'$  and  $\Phi$  are summable so that if  $a$  is a point in the interior of the interval where  $f'$  and  $\Phi$  are given, we may put

$$\psi(x) = \int_a^x f' \Phi.$$

If  $x_0$  is another point in the interior of the interval and if the same holds good for  $x_0 + h$ , we have

$$\begin{aligned} \frac{1}{h} \left\{ \psi(x_0+h) - \psi(x_0) \right\} &= \frac{1}{h} \int_{x_0}^{x_0+h} f' \Phi = \frac{\Phi(x_0)}{h} \int_{x_0}^{x_0+h} f' + \frac{1}{h} \int_{x_0}^{x_0+h} \{ \Phi - \Phi(x_0) \} f' = \\ &= \Phi(x_0) \frac{f(x_0+h) - f(x_0)}{h} + \frac{\theta}{h} \int_{x_0}^{x_0+h} |\Phi - \Phi(x_0)| \cdot |f'| \quad ; \quad |\theta| \leq 1 \quad (1) \end{aligned}$$

The first term of (1)  $\rightarrow 0$  for  $h \rightarrow 0$ .

In case *A* we have

$$|\Phi - \Phi(x_0)| < K|h|,$$

where *K* can vary with  $x_0$  but does not depend on  $h$ . Hence the absolute value of the second term of (1) is less than that of  $K \int_{x_0}^{x_0+h} |f'|$ , and,  $f'$  being summable, this integral has zero as limit for  $h \rightarrow 0$ . In this way we have proved that  $\Phi(x_0) f'(x_0) = \psi'(x_0)$ .

4. In case *B* we choose a positive number  $\epsilon$  and divide the interval  $I(x_0, x_0 + h)$  into the two sets of points  $I_1$  containing the points where  $|\Phi - \Phi(x_0)| < \epsilon$  and  $I_2$  containing the points where  $|\Phi - \Phi(x_0)| \geq \epsilon$ . If  $\mu I_2$  is the measure of  $I_2$ , the approximative continuity of  $\Phi$  means:

$$\frac{1}{h} \mu I_2 \rightarrow 0 \text{ for } h \rightarrow 0. \dots \dots \dots (2)$$

If *M* is the upper limit of  $|f'|$  we have

$$\frac{1}{|h|} \int_{I_1} |\Phi - \Phi(x_0)| \cdot |f'| \leq \frac{\epsilon}{|h|} \int_{I_1} |f'| \leq \frac{\epsilon M}{|h|} \mu I_1 \leq \epsilon M \dots (3)$$

If *N* is the upper limit of  $|\Phi|$  we have

$$\frac{1}{|h|} \int_{I_2} |\Phi - \Phi(x_0)| \cdot |f'| \leq \frac{2MN}{|h|} \mu I_2 \rightarrow 0 \text{ for } h \rightarrow 0. \dots (4)$$

According to (3) and (4) the second term of (1) has the limit zero for  $h \rightarrow 0$ , hence  $\Phi(x_0) f'(x_0) = \psi'(x_0)$ .

5. In order to prove theorem *C* we consider the function

$$f(x) = \int_0^x |t|^{-\frac{1}{2}} \sin \frac{1}{t} dt.$$

For  $x \neq 0$  we have

$$f'(x) = |x|^{-\frac{1}{2}} \sin \frac{1}{x} \dots \dots \dots (5)$$

Further for  $x \neq 0$

$$\begin{aligned} \left| \frac{f(x) - f(0)}{x} \right| &= \frac{1}{|x|} \left| \int_0^x |t|^{-\frac{1}{2}} \sin \frac{1}{t} dt \right| = \frac{1}{|x|} \left| \int_0^{|x|} t^{-\frac{1}{2}} \sin \frac{1}{t} dt \right| = \\ &= \frac{1}{|x|} \left| \int_{\frac{1}{|x|}}^{\infty} u^{-\frac{3}{2}} \sin u du \right|. \end{aligned}$$

By applying the second theorem of the mean we find

$$\left| \frac{f(x) - f(0)}{x} \right| = |x|^{\frac{1}{2}} \left| \int_{\frac{1}{|x|}}^{\xi} \sin u \, du \right| < 2 |x|^{\frac{1}{2}} \rightarrow 0 \text{ for } x \rightarrow 0. \quad (6)$$

From (5) and (6) follows

$$f'(x) = |x|^{-\frac{1}{2}} \sin \frac{1}{x}, \quad x \neq 0,$$

$$f'(0) = 0.$$

From  $|f'| < |x|^{-\frac{1}{2}}$ ,  $x \neq 0$  it follows that  $f'$  is summable.

Further  $x=0$  is the only point of discontinuity of  $f'$ .

If we consider the continuous function

$$\Phi(x) = |x|^{\frac{1}{2}} \sin \frac{1}{x}, \quad x \neq 0$$

$$\Phi(0) = 0,$$

we have

$$\left. \begin{aligned} f'(x) \Phi(x) &= \sin^2 \frac{1}{x}, \quad x \neq 0 \\ f'(0) \Phi(0) &= 0 \end{aligned} \right\} \dots \dots \dots (7)$$

$$\text{Be } F(x) = \int_0^x f'(t) \Phi(t) \, dt = \int_0^x \sin^2 \frac{1}{t} \, dt.$$

For  $x \neq 0$  we have

$$F'(x) = \sin^2 \frac{1}{x} = f'(x) \Phi(x) \quad \dots \dots \dots (8)$$

Further for  $\frac{1}{k\pi} < |x| \leq \frac{1}{(k-1)\pi}$ ,  $k$  integer and  $\geq 2$ :

$$\begin{aligned} \frac{F(x) - F(0)}{x} &= \frac{1}{x} \int_0^x \sin^2 \frac{1}{t} \, dt = \frac{1}{|x|} \int_0^{|x|} \sin^2 \frac{1}{t} \, dt > (k-1)\pi \int_0^{\frac{1}{k\pi}} \sin^2 \frac{1}{t} \, dt = \\ &= (k-1)\pi \int_{k\pi}^{\infty} \frac{\sin^2 u \, du}{u^2} = (k-1)\pi \sum_{n=k}^{\infty} \int_{n\pi}^{(n+1)\pi} \frac{\sin^2 u \, du}{u^2} > \\ &> (k-1)\pi \sum_{n=k}^{\infty} \frac{1}{(n+1)^2 \pi^2} \int_0^{\pi} \sin^2 u \, du = \frac{k-1}{2} \sum_{n=0}^{\infty} \frac{1}{(n+1)^2} > \frac{k-1}{2(k+1)}. \end{aligned}$$

And

$$\begin{aligned} \frac{F(x)-F(0)}{x} &< k\pi \int_0^{\frac{1}{(k-1)\pi}} \sin^2 t \frac{1}{t} dt = k\pi \int_{(k-1)\pi}^{\infty} \frac{\sin^2 u}{u^2} du = \\ &= k\pi \sum_{n=k-1}^{\infty} \int_{n\pi}^{(n+1)\pi} \frac{\sin^2 u}{u^2} < k\pi \sum_{n=k-1}^{\infty} \frac{1}{n^2 \pi^2} \int_0^{\pi} \sin^2 u du = \frac{k}{2} \sum_{n=k-1}^{\infty} \frac{1}{n^2 \pi^2} < \frac{k}{2(k-2)}. \end{aligned}$$

For  $x \rightarrow 0$  we have  $k \rightarrow \infty$ , hence

$$F'(0) = \frac{1}{2} \dots \dots \dots (9)$$

From (8) and (9) follows that  $F$  has everywhere a derivative, to wit  $\sin^2 \frac{1}{x}$  for  $x \neq 0$  and  $\frac{1}{2}$  for  $x = 0$ .

If now  $f'\Phi$  were a derivative,  $F' - f'\Phi$  would also be a derivative, these functions being finite. But according to (7), (8) and (9)  $F' - f'\Phi = 0$  for  $x \neq 0$  and  $= \frac{1}{2}$  for  $x = 0$ ; consequently this function is no derivate.

$f'\Phi$  is, therefore, no derivative (although its integral  $F$  has a limited derivative). As  $f'$  is summable, has only one point of discontinuity, and  $\Phi$  is continuous, we have proved theorem C.

*Utrecht, Jan. 12, 1925.*

**Chemistry.** — „*Decomposition of Paraffin Wax at 450° C. in Presence and in Absence of Hydrogen under High Pressure.*” By Prof. H. I. WATERMAN and J. N. J. PERQUIN, chem. eng. (Communicated by Prof. J. BÖESEKEN).

(Communicated at the meeting of February 28, 1925.)

Earlier investigations have shown the favourable influence of hydrogen under high pressure on the process of decomposition which occurs when paraffin wax is heated to 450° C. It was found that hydrogen under high pressure :

- a. Enters into combination, and forms part of the products, during the reactions which are proceeding.
- b. Causes the production of less unsaturated distillates (gasoline and kerosene).
- c. Lowers the specific gravity of the residue obtained on distillation of the reaction-product.

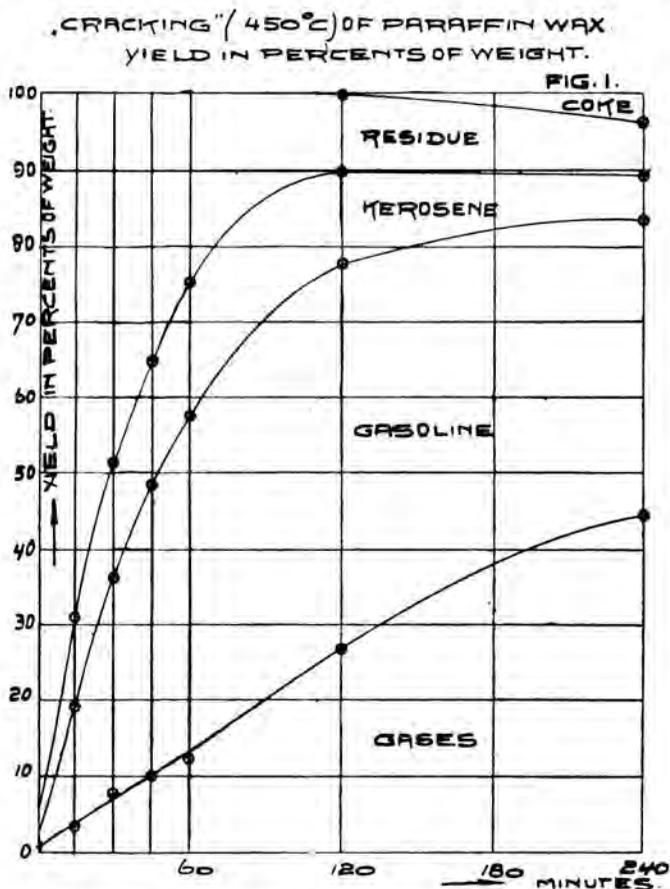
Notwithstanding the lack of experimental data and our imperfect knowledge of the reactions which occur, we have been successful in adding to our knowledge of the Berginisation process. We have reached this result by studying the influence of time on the decomposition at 450° C. of paraffin wax in the presence and in the absence of hydrogen under high pressure. The raw material which was used in these experiments was Rangoon paraffin, solidifying point (SHUKOFF) 58°, specific gravity 20°/4° : 0.913. Elementary analysis gave 84.6 per cent. C. and 14.8 per cent. H. The charge for each experiment was 200 grams ; this was heated at 450° C. in the autoclave already described by us <sup>1)</sup>. To promote mixing, three steel balls of a total weight of 79.5 grams were added. The chief results are shown in the appended table.

*The Influence of Time on the Decomposition of Paraffin Wax at 450° C. without the Addition of Hydrogen („Cracking”).*

The quantity of gas produced and the maximum pressure reached increase with time of heating ; the pressure after cooling and the volume of gas obtained likewise increase. The volume of „heavy hydrocarbons” also increases to a determined limit and in experiment 92 this maximum is reached. The quantity of hydrogen liberated increases regularly, while the average number of atoms of carbon per molecule of the methane hydrocarbons obtained does not show much variation ; it decreases from 2.4 to 2.1. Only traces of coke are formed at first. After two hours

<sup>1)</sup> Journ. of the Institution of Petrol. Technologists, Vol. 10, N<sup>o</sup>. 45, Sept. 1924, p. 671—672. These Proceedings 27, p. 83 (1923—24).

(experiment 92) 0.3 per cent. of „carbon” is found ; but, after 4 hours, this has increased to 4.0 per cent. in the case of experiment 94. Our experiments indicate that the process is a normal one ; the paraffin hydrocarbons break down, immediately forming decomposition products such as the lower

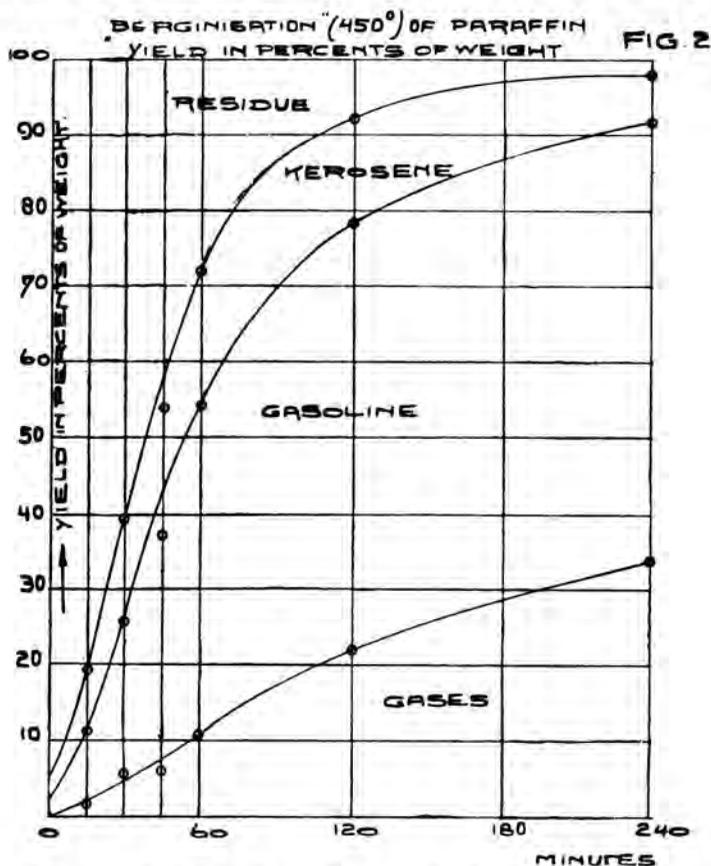


hydrocarbons (ethane and probably methane), and hydrogen. Since the liberation of „carbon” is not immediate, but takes place subsequently with great rapidity, it must do so at the expense of the products of decomposition, and not of the hydrocarbons present in the unaltered paraffin wax itself. The oil produced by short periods of heating solidifies completely at ordinary temperatures, while with longer periods the product becomes more liquid, notwithstanding the formation of considerable quantities of gas. At first the specific gravity diminishes rapidly, until after about one hour's heating the minimum is reached (No. 89, 0.767 ; No. 92, 0.766). Thereafter the liberation of „carbon” begins and at the same time the specific gravity of the oil rises (No. 94, 0.777).

The liquid product becomes progressively richer in gasoline although the absolute yield of gasoline (Fig. 1) after a rapid initial increase diminishes after two hours (after 2 hours, 50.6 per cent. ; after 4 hours, 38.9 per cent).

The percentage of kerosene in the liquid product diminishes after the first hour, as does the percentage yield (Fig. 1). The quantity of residue boiling above  $300^{\circ}$  C. diminishes continuously with the percentage yield (Fig. 1).

These facts show that at first gas, gasoline and kerosene increase at the



expense of the residue, but that subsequently the kerosene and gasoline at first formed diminish with the residue. As a result it is only the yield of gas which increases, with accompanying liberation of „carbon”. It must be understood that none of the fractions mentioned remains unaltered during the process. The whole system, excluding such constituents as hydrogen and methane, is in a condition of continual decomposition. This is proved by the decrease in the bromine values of the oil produced (7.5, 19.6, 25.1, 27.5, 27.4, 23.0, and 17.5 after 1, 15, 30, 45, 60, 120 and 240 minutes respectively). This decrease occurs after a preliminary increase (Fig. 3). The quantity of heavy hydrocarbons in the gas at first rises, but after two hours begins to fall, with an accompanying decline in the bromine value. The lowering of the bromine value is probably not due to the formation of gaseous unsaturated products such as ethylene, but rather to the occurrence of polymerisation. In this connection it is interesting to note that the specific gravity of the residue from the oil produced by cracking decreases

at first, and afterwards increases rapidly, finally becoming greater than unity (Fig. 4). It has already been mentioned that the specific gravity of the liquid product of the cracking experiments rises with prolonged treatment (Fig. 4).

*The Influence of Time on the Decomposition at 450° C. of Paraffin Wax in the Presence of Hydrogen under High Pressure (Bergius Process).*

In these experiments the autoclave was charged with hydrogen to 110 kg per sq. cm. before heating. The maximum pressures reached indicate a course of events different from that obtained in the cracking experiments. The maximum pressures 210.5 and 218 kg. per sq. cm. in experiments 99 and 106 are apparently caused merely by the rise in temperature, for decomposition and liberation of gas have hardly begun. Experiments 103.

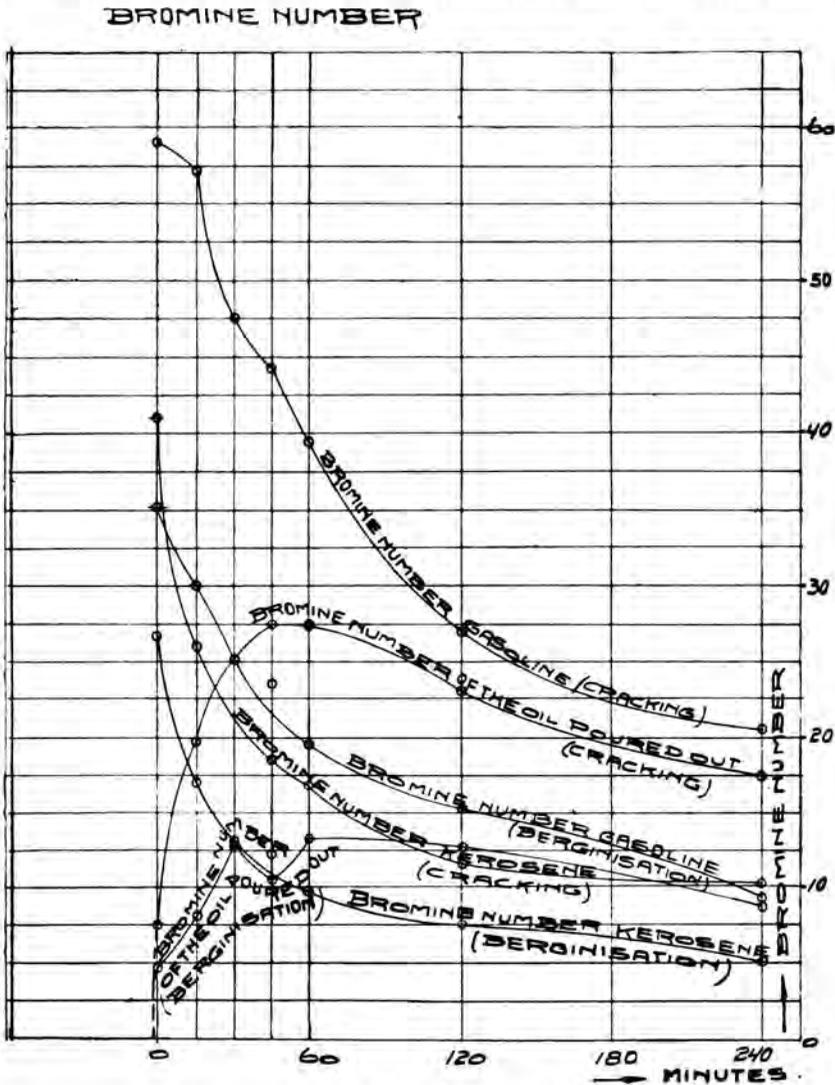


Fig. 3.

No.	Readings during the experiment						Ingoing Material			Product (per cent. on wax charged)				Analysis of the				
	Time to reach reaction temp. (min.)	Time at reaction temp. (min.)	Initial pressure (kg. per sq. cm.)	Maximum pressure (kg. per sq. cm.)	Pressure cold (kg. per sq. cm.)	Temperature during reaction (° c.)	Wax (g.)	Gas (g.)	Gas (per cent. on wax).	Oil	Gas	"Carbon"	Loss (calculated)	Specific gravity	ENGLER			
															Per cent. by weight on liquid product			
					Gasoline to 220° c.	Kerosene 220—300° c.	Residue above 300° c.	Loss										
99	25	1	110	210.5	105	450°	200	11.4	5.7	99.7	6.1		—	—	—	—	—	
106	29	1	110	218		450°	200	12.7	6.3	99.7	6.6		—	2.3	2.4	94.8	0.5	
107	26	1	0	6.2	0.6	450°	200	0	0	99.3	0.7		0.884	2.5	2.9	94.2	0.4	
103	23	15	110	220	106.5	450°	200	12.4	6.2	98.5	7.7		—	9.3	8.4	81.7	0.6	
108	30	15	0	16.3	2.7	450°	200	0	0	96.8	2.2	0	1.0	0.831	15.1	12.2	71.4	1.3
104	30	30	110	223	104	450°	200	12.7	6.3	94.5	9.2		2.6	0.819	20.3	14.3	64.2	1.2
109	25	30	0	28.4	4.8	450°	200	0	0	92.5	4.3		3.2	0.781	28.2	16.3	52.8	2.7
102	26	45	110	219	100	450°	200	12.7	6.3	94.3	9.2		2.8	0.755	30.6	18.0	48.8	2.6
111	39	45	0	37	6.2	450°	200	0	0	90.0	6.7		3.3	0.771	38.5	18.3	39.2	4.0
74	28	60	110	224	95	450°	200	11.6	5.8	89.5	14.2		2.1	0.741	46.9	19.7	29.6	3.8
76	36	60	110	222	96	450°	200	11.5	5.8	89.5	13.1	0	3.2	0.746	44.5	19.8	33.5	2.2
89	28	60	0	48	8	450°	200	0	0	87.7	11.0		1.3	0.767	47.9	19.9	28.8	3.4
80	30	120	110	223	85.5	450°	200	11.6	5.8	78.0	22.2	0	5.6	0.718	67.8	17.5	10.0	4.7
78	32	60	110	228	85	460°	200	11.6	5.8	77.0	23.7	0	5.1	0.719	69.0	16.9	9.5	4.6
92	25	120	0	68	16	450°	200	0	0	73.0	21.9	0.3	4.8	0.766	65.8	16.6	14.0	3.6
87 <sup>1)</sup>	25+27	240	110	260 (220.5)	90.5 (82)	450°	200	15.2	7.6	65.7	35.5	0	6.4	0.703	83.0	9.5	2.5	5.0
94 <sup>1)</sup>	23+25	240	0	90 (70.2)	24.5 (15.8)	450°	200	0	0	51.5	37.8	4.0	6.7	0.777	71.9	11.3	13.1	3.7
72	20	60	110	222.5	102	450°	100	12.9	12.9	87.5	20.8	0	4.6	—	36.3	18.4	43.5	1.8
68	27	60	110	220	92.5	450°	300	9.7	3.2	93.3	7.7	0	2.2	0.753	36.6	19.7	39.6	4.1

<sup>1)</sup> In these experiments the heating was interrupted half way through, the autoclave was cooled (pressures 82 and 15.8 kg. per sq. cm. respectively), hydrogen was added, in the case of experiment 87, to 110 kg. per sq. cm. (none was added in the case of experiment 94) and the heating resumed. The maximum pressures then attained were 260 and 90 kg. per sq. cm. respectively; 220.5 and 70.2 kg. per sq. cm. had been reached in the first period of heating.

Liquid Product				Gas														Hydrogen fixed	
Distillation				Bromine value (addition)			Gas charged (litres)		Gas obtained (litres) <sup>3)</sup>										
Loss	Gasoline + Loss	Kerosene	Residue				Hydrogen	Oxygen	Total	Heavy hydro-carbons	Oxygen	Carbonmonoxide	Hydrogen	Other hydro-carbons	Nitrogen	C-atoms (av.) in other hydro-carbons	In g.		
—	—	—	—	—	—	—	105.2	1.4	106.8	—	1.0	0.0	104.5	0.3	0.6	—	—	—	
2.8	2.8	2.4	94.5	4.8	35.1	26.6	109.7	2.0	112.4	0	2.0	0.0	109.0	0.4	1.0	4.4	—	—	
2.9	2.9	2.9	93.6	7.5	59.2	41.0	0	0	1	0.1	0.0	0.0	0.2	0.2	0.4	2.4	—	—	
9.9	9.7	8.3	80.5	8.2	30.0	16.9	106.9	2.0	104.6	0	0.2	0.4	101.4	1.8	0.8	3.0	0.5	0.3	
6.4	15.9	11.8	69.1	19.6	57.4	26.0	0	0	3.2	0.6	0	0.0	0.3	1.3	0.8	2.3	—	—	
1.5	20.3	13.5	60.7	12.8	25.0	13.1	109.4	2.0	104.4	0	0.4	0.4	98.8	3.1	1.7	3.0	0.9	0.5	
0.9	28.6	15.1	48.8	25.1	47.6	20.8	0	0	5.8	1.3	0.0	0.1	0.7	3.9	0.7	2.2	—	—	
3.2	31.3	17.0	46.0	10.5	23.5	12.3	110.1	2.0	96.5	0.2	0.8	0.1	88.4	3.5	3.5	2.5	1.9	1.0	
2.5	38.2	16.5	35.2	27.5	44.3	18.5	0	0	10.4	2.4	0.1	0.1	1.0	5.7	1.0	2.2	—	—	
0.7	45.4	17.6	26.5	13.8	19.7	9.9	113.0	1.0	100.0	0.6	0.8	0.0	87.7	9.1	1.8	2.2	2.3	1.2	
6.7	41.8	17.7	30.0	12.8	19.2	9.8	112.1	1.0	98.5	0.8	0.4	0.6	87.0	8.4	1.5	2.2	2.2	1.1	
1.3	45.0	17.4	25.3	(27.4) <sup>2)</sup>	39.4	16.8	0	0	18.9	3.5	0.2	0.2	1.9	12.5	0.6	2.1	—	—	
2.5	56.6	13.7	7.8	12.8	15.3	7.6	113.8	1.0	101.0	1.0	0.4	0.7	77.0	20.4	1.5	2.5	3.3	1.6	
3.6	56.7	13.0	7.3	15.0	17.4	8.3	113.0	1.0	100.5	1.3	0.6	0.5	75.3	21.2	1.6	2.4	3.4	1.7	
9.4	50.6	12.1	10.2	(23.0) <sup>2)</sup>	27.7	11.7	0	0	32.5	4.3	0.5	0.4	2.3	23.7	1.3	2.2	—	—	
18.0	57.8	6.2	1.6	8.8	9.5	5.2	142.0	1.7	116.4	1.4	0.9	0.8	76.2	35.4	1.7	2.5	5.9	2.9	
75.6	38.9	5.8	6.7	(17.5) <sup>2)</sup>	20.5	10.3	0	0	55.6	3.2	0.4	0.4	3.4	47.8	0.4	2.1	—	—	
38.1	33.3	16.1	38.1	—	18.3	10.1	126.4	1.1	115.5	0.6	0.8	0.5	107.5	4.7	1.4	2.1	1.7	1.7	
40.7	38.0	18.4	36.9	14.3	22.1	11.3	103.1	0.3	86.5	0.9	0.5	0.3	74.5	7.8	2.4	2.4	2.6	0.9	

<sup>2)</sup> Approximate determinations.

<sup>3)</sup> CO<sub>2</sub> absent.

SPECIFIC WEIGHT (120°C) OF THE OIL POURED OUT  
AND OF THE RESIDUE OF ENGLER DISTILLATION

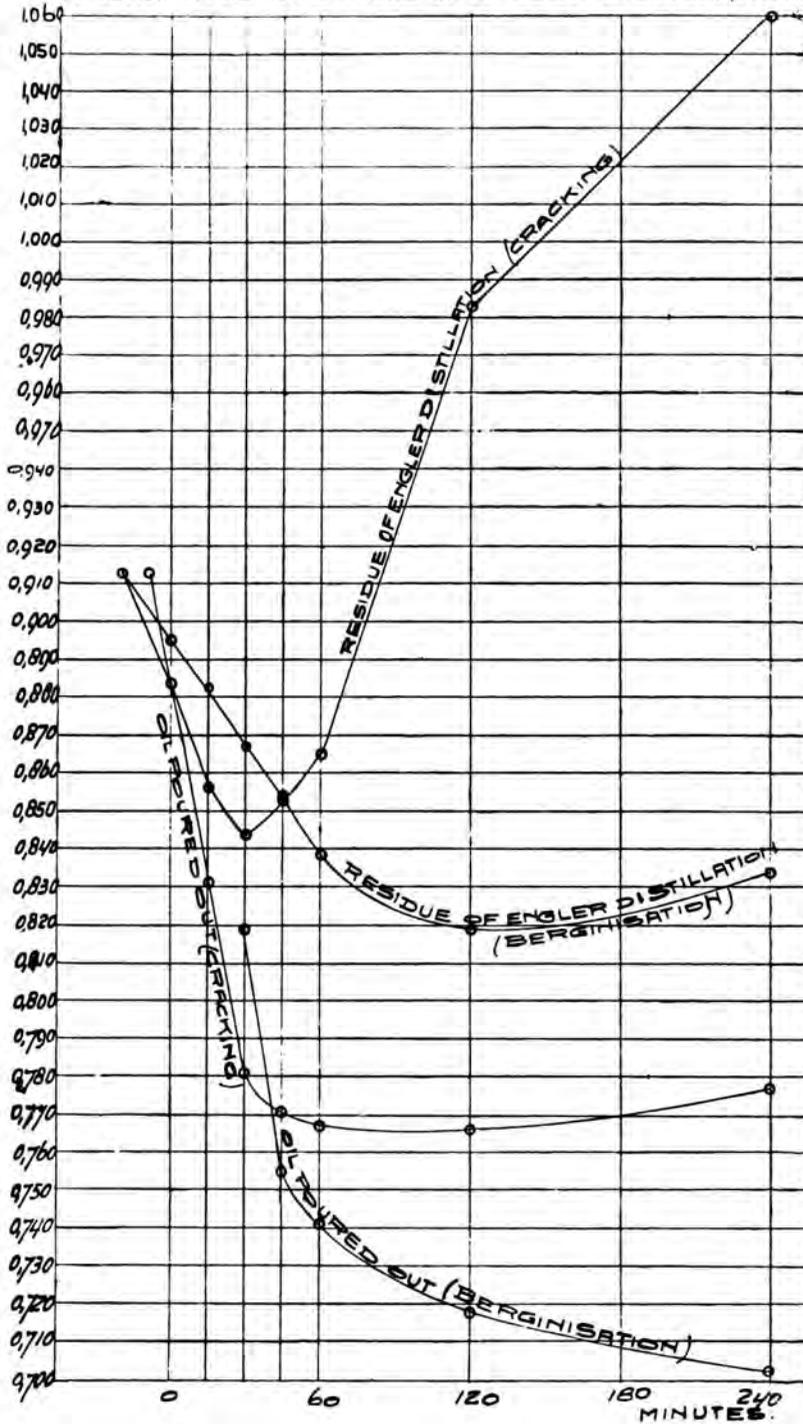


Fig. 4.

104, 102, 74, 76 and 80 after 15, 30, 45, 60, 60 and 120 minutes respectively, notwithstanding the decomposition which is taking place, give maximum pressures which are scarcely higher than those in experiments 99 and 106. This is doubtless because the effect of hydrogenation is becoming important. Confirmation is provided by the observed final pressures, which are smaller in proportion to the duration of the experiment. From the volume and composition of the gas obtained it follows that in experiments 103, 104, 102, 74, 76 and 80, and in 87 (where hydrogen was added twice), 0.3, 0.5, 1.0, 1.2, 1.1, 1.6 and 2.9 per cent. by weight of hydrogen respectively (calculated on the paraffin wax) are fixed. The bromine values of the original oil produced and of the corresponding gasoline and kerosene (Fig. 3) show that the bromine value is always lower than in the corresponding cracking experiments. A point of even greater importance is that after 60 and up to 120 minutes' Berginisation there is no decrease in the bromine value of the oil produced, as there is in the analogous cracking experiments. From this it may be concluded that probably polymerisation does not occur in these Berginisation experiments. It is only after further heating that the bromine value of the oil diminishes. Fig. 4 shows that after 120 minutes the specific gravity of the Engler distillation residue increases; up to 120 minutes' Berginisation this specific gravity diminishes.

The high hydrogen pressures used in Berginisation may be expected to modify the cracking process. A lower proportion of heavy hydrocarbons will be formed; in 99, 106, 103, 104, 102, 74, 76, 80 and 87, there are produced 0.0, 0.0, 0.0, 0.0, 0.2, 0.6, 0.8, 1.0 and 1.4 L. respectively. The longer the experiment lasts, the larger this quantity. This holds for the methane hydrocarbons also. In the Berginisation process there is less decomposition, for the average number of atoms of carbon per molecule, although it continuously diminishes, always remains greater than in the corresponding cracking experiments.

The change in the yields of gas, gasoline, kerosene and residue (Fig. 2) is an interesting result of Berginisation. The whole process is characterized by the formation of gas and gasoline and at first of kerosene, at the expense of the residue. Later, the percentage of kerosene diminishes. In our experiments the percentage of gasoline increased continuously. It is an important point that finally the residue almost wholly disappeared, so that only gases, gasoline and kerosene were left. The origin of the gasoline must be looked for in the cracking which is taking place.

These observations show that Berginisation results in a modification of the cracking process, gas and gasoline being formed initially in smaller quantity and of a less unsaturated character than the corresponding products of cracking. The falling off in the bromine value of the oil produced after a certain period of heating, and the continuous decline in the bromine value of the gasoline and kerosene, observed even more clearly in cracking than in Berginisation, must be attributed to the rupture of double bonds, followed by polymerisation in the case of cracking and, it may be

supposed, by hydrogenation of the portions of the molecule, so that polymerisation is prevented or modified, in the case of Berginisation. This must be in close connection with the fact that in our Berginisation experiments practically no carbon (coke) is formed. The breaking up of molecules must take place throughout Berginisation, as otherwise the increase in the yield of gasoline, which finally exceeds that in the corresponding cracking experiments, could not be explained.

The direct addition of hydrogen to unsaturated hydrocarbons already present is not probable, because no catalyst is added and because the temperature is so high that in many cases the tendency is towards a decomposition of the corresponding saturated hydrocarbon into hydrogen and the unsaturated hydrocarbon rather than towards a reaction in the reverse sense, although this decomposition will be modified by the presence of hydrogen under high pressure. We hope to deal with this subject in more detail at a later date.

The advantage of Berginisation as compared with cracking appears

Nature of the Product and of the Distillation Residue.

Experiment	Minutes heating after the reaction temperature has been reached	Product	Residue
106	1	S <sub>pw</sub>	S <sub>pw</sub>
107	1	S <sub>pw</sub>	S <sub>pw</sub>
103	15	S <sub>pw</sub>	S <sub>pw</sub>
108	15	S <sub>pw</sub>	S <sub>pw</sub>
104	30	S <sub>pw</sub>	S <sub>pw</sub>
109	30	S <sub>v</sub>	S <sub>v</sub>
102	45	S <sub>pw</sub>	S <sub>pw</sub>
111	45	L (dark)	S <sub>v</sub>
74	60	S <sub>pw</sub>	S <sub>pw</sub>
89	60	L (dark)	S <sub>v</sub>
80	120	L (clear)	S <sub>pw</sub>
78	60 (temp. 460°)	L (clear)	S <sub>pw</sub>
92	120	L (dark)	L (dark)
87	240	L (clear)	L (dark)
94	240	L (dark)	L (dark)

S<sub>pw</sub> = solid, like paraffin wax.

L (dark) = liquid, dark.

S<sub>v</sub> = consistency of vaseline.

L (clear) = liquid, clear.

distinctly from the elementary composition of the residue in the two processes. For instance, in experiment 87 the composition of the residue was 85.4 per cent. carbon and 13.8 per cent. hydrogen, in 94 91.8 per cent. of carbon and 8.2 per cent. of hydrogen, respectively; in other words, Berginisation prevents loss of hydrogen from the residues. This is of considerable importance, the process of cracking always giving oils or residues which are poorer in hydrogen, because in the gases formed,  $H_2$ ,  $CH_4$ ,  $C_2H_6$ , etc., an excess of hydrogen is present. This loss of hydrogen to some extent takes place during Berginisation, but in this process the loss of hydrogen is supplied from outside. The advantage of Berginisation is, therefore, proved. It is true that the hydrogen introduced from the outside is later found wholly or partly in the gases, but this supply of hydrogen has prevented a too extensive removal of hydrogen from the hydrocarbons. The great influence of temperature is shown by a comparison of experiments 78 and 80. In experiment 78 the temperature was ten degrees higher, and the effect was that in half the time (60 minutes in 78 and 120 minutes in 80) nearly the same result was obtained. Analogous observations were made by Dr. A. E. DUNSTAN<sup>1</sup>). The ten degrees higher temperature has apparently doubled the velocity of the complex of reactions. This fact being mentioned it must be added that without a more detailed study of this subject there is not much matter for discussion on the theoretical significance of this observation. That the quantity of paraffin wax used has a great influence appears from experiments 72 and 68, in which the percentage of fixed hydrogen is quite different. It is necessary, therefore, always to work under completely comparable conditions.

*Summary.* Comparative experiments show that Berginisation has various advantages over heating in absence of hydrogen under high pressures (cracking). After some hours' Berginisation a larger percentage of gasoline and of kerosene is obtained, while less gas is produced. Coke has not been formed to any material extent. The liquid products of reaction are more saturated. The residue on distillation (boiling point exceeding  $300^\circ C.$ ) after 4 hours' Berginisation is but small. On the other hand, it must be observed that in Berginisation less gasoline and correspondingly less gas is formed initially than in the corresponding cracking experiments. In Berginisation cracking is restricted and the very reactive residues produced by cracking are converted into hydrocarbons of the gasoline and kerosene distillates. Polymerisation and the formation of coke from the unsaturated residues is thus prevented or diminished. While cracking gives rise to residue poor in hydrogen, Berginisation prevents the loss of hydrogen from residues. In one Berginisation experiment a residue was obtained which gave 13.8 per cent. of hydrogen, whereas the raw material contained 14.8 per cent. In a corresponding cracking experiment the residue contained only 8.2 per cent. of hydrogen.

<sup>1</sup>) Journ. Institution Petroleum technol. 10, 728 (1924).

Berginisation must be considered as a combined cracking and hydrogenation process. The useful feature of cracking, the breaking down of hydrocarbon molecules, remains, but is made more regular, while the products are obtained in a more stable condition on account of the addition of hydrogen, so that extensive polymerisation and formation of coke are avoided. The main feature of Berginisation is, therefore, not the saturation of unsaturated hydrocarbons already present. In this respect it differs widely from the ordinary hydrogenation of vegetable or animal oils, which is conducted in the presence of catalysts.

This investigation clears up the scientific significance of the Bergius hydrogenation process.

In continuation of this research the isolation, as far as possible, of the chemical compounds formed will be attempted, while our results on the hydrogenation of coal by the Bergius method will be published shortly.

We wish to express our thanks to Mr. A. C. OUBORG, who assisted us during the course of these investigations.

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**Microbiology.** — A. J. KLUYVER and H. J. L. DONKER: "*The unity in the chemistry of the fermentative sugar dissimilation processes of microbes.*" (Communicated by Prof. G. VAN ITERSON JR.).

(Communicated at the meeting of November 29, 1924).

### § 1. *Introduction.*

Elsewhere <sup>1)</sup> one of us has elucidated how in metabolism of microbes two processes may be distinguished: dissimilation and assimilation, which respectively meet the energetic and material needs of the organism. In the same place it is further pointed out how two types have to be distinguished in the mode of energy supply, namely, those where the energy is derived from an oxidation with the absorption of free oxygen and those where the energy is derived from chemical reactions, in which free oxygen plays no part. These types of dissimilation are distinguished as oxidative and fermentative.

The sugar dissimilation processes brought about by microbes are of theoretical as well as of great practical importance. When one tries to obtain a summary of these processes based on the relative data in literature, it appears to be very difficult. One obtains the impression that among sugar fermenting microbes an almost unending variety of manifestations of life is present.

On the one hand this finds its cause in the fact that most microbes are described absolutely without any mutual relation, that is to say, without taking into account the natural relationships amongst microbes.

On the other hand this is a consequence of an almost complete lack of insight by the majority of investigators into the chemistry of the processes just mentioned.

In this communication we shall endeavour to bring order into this chaos of phenomena.

### § 2. *The classification of all sugar fermenting microbes into a limited number of natural groups.*

In the first place we will look into the question, how far it is possible to collect together the organisms under consideration into a number of natural groups according to their relationship.

<sup>1)</sup> A. J. KLUYVER, Chem. Weekblad Vol. 21, p. 66. (1924).

TABLE I. SUMMARY OF THE GROUPS OF SUGAR-FERMENTING MICROBES AND THEIR CHARACTERISTIC PROPERTIES.

GROUPS.	MOST IMPORTANT PRODUCTS OF THE FERMENTATIVE SUGAR DISSIMILATION.	REMAINING CHARACTERISTICS.	EXAMPLES BELONGING TO THE VARIOUS GROUPS.
I. Alcohol yeasts.	Alcohol, carbon dioxide.	General properties of the Ascomycetes and related Fungi imperfecti.	<i>Saccharomyces cerevisiae</i> (Meyen) etc.
II. True lactic acid bacteria.	Lactic acid alone or together with acetic acid, alcohol, glycerol and carbon dioxide.	Gram positive, catalase negative, lack cilia. Do not form spores. Unable to synthesise protein from simpler nitrogen compounds.	<i>Lactobacillus Delbrücki</i> (Leichmann), <i>Lactobacillus fermentum</i> (Beijerinck) <i>Streptococcus lacticus</i> (Kruse), <i>Streptococcus pyogenes</i> (Rosenbach), <i>Streptococcus mastitidis</i> (Guillebeau), <i>Bacillus mannicus</i> (Gayon et Dubourg), <i>Lactobacillus pentoaceticus</i> (Peterson et Fred), <i>Leuconostoc mesenterioides</i> (Van Tieghem) <i>Bacterium gracile</i> (Müller-Thurgau et Osterwalder) etc.
III. True propionic acid bacteria.	Propionic acid, lactic acid, acetic acid and carbon dioxide.	As II but generally branched forms.	<i>Bacterium acidi propionici</i> (Freudenreich et Orla-Jensen) etc.
IV. Coli bacteria in the widest sense. ( <i>Aerobacter</i> , Beijerinck).	Lactic acid, acetic acid, alcohol, sometimes 2-3 butylene glycol, formic acid. If gas always hydrogen along with carbon dioxide.	Gram negative, catalase positive, rod form with peritrichic cilia. Form no spores.	<i>Bacillus coli commune</i> (Escherich), <i>Bacillus lactis aerogenes</i> (Escherich), <i>Bacterium aerogenes</i> (American investigators), <i>Bacillus typhi</i> (Eberth), <i>Bacillus cloacae</i> (Jordan), <i>Bacillus ethaceticus</i> (Frankland), <i>Bacillus pneumoniae</i> (Friedländer), <i>Bacterium herbicola</i> (Burri et Duggeli), <i>Micrococcus prodigiosus</i> (Cohn), <i>Bacterium levans</i> (Wolffin) etc.
V. <i>Proteus</i> -bacteria.	As IV.	As IV but more adapted to the fermentative dissimilation of the hydrolytic decomposition products of proteins.	<i>Bacillus proteus vulgaris</i> , (Hauser) etc.
VI. Facultative anaerobic sugar fermenting spore forming bacteria.	Besides acetic and alcohol either 2-3 butylene glycol or acetone, carbon dioxide and hydrogen.	As IV but spore forming, generally granulose as reserve material.	<i>Clostridium polymyxa</i> (Prazmowski) = <i>Granulobacter polymyxa</i> (Beijerinck) = <i>Bac. polymyxa</i> (Beijerinck), <i>Bacillus macerans</i> (Schardinger), <i>Bacillus asterosporus</i> (A. Meyer), <i>Bacillus acetothylicum</i> (Northrop and others) etc.
VII. True butyric acid and butyl alcohol bacteria.	Butyric acid, acetic acid, butyl alcohol, isopropyl alcohol, acetone; carbon dioxide and hydrogen.	Obligate anaerobic. Catalase negative, form spores, rod with peritrichic cilia. Granulose as reserve material.	<i>Bacillus amylobacter</i> (Gruber), <i>Bacillus amylozyma</i> (Perdrix), „Beweglicher Buttersäurebazillus" (Graszberger und Schattenfroh) <i>Granulobacter saccharobutyricum</i> (Beijerinck), <i>Granulobacter butylicum</i> (Beijerinck), <i>Granulobacter pectinovorum</i> (Beijerinck), <i>Clostridium pastorianum</i> (Winogradsky), <i>Bacillus granulobacter pectinovorum</i> (Speakman) etc.
VIII. Butyric acid and butyl alcohol bacteria of the paraputrificus group.	As VII.	As VII but more adapted to the fermentative dissimilation of the hydrol. decomposition prod. of proteins	<i>Bacillus sporogenes enteritidis</i> (Klein), <i>Bacillus bifermentans sporogenes</i> (Tissier et Martelly), <i>Bacillus paraputrificus</i> (Bienstock), „Unbeweglicher Buttersäurebazillus" (Graszberger and Schattenfroh), <i>Bacillus oedematis maligni</i> (Pasteur et Joubert), <i>Bacillus hotulinus</i> (Van Ermenghem) etc.

The relationship of the species belonging to one natural group should manifest itself both in the more important morphological and in the more essential physiological properties. In this connection no or at least far too little notice has been taken of the physiological properties by former investigators and there is no doubt that this circumstance is to a large extent the cause of the general chaos still prevailing.

This consideration has been ably put forward as far back as 1909 by ORLA-JENSEN in his „Hauptlinien des natürlichen Bakteriensystems“<sup>1)</sup>. As this investigator mentions, in the classification of bacteria one must, to quote verbally, „mehr Gewicht auf die inneren Eigenschaften als auf die äüßere Form legen“.

Without doubt metabolism occupies an important place among these inner properties. The chemical changes essential for the maintenance of life are nothing but a reflection of the chemical configuration of the living protoplasm on the nutriments offered or in other words: similar metabolism is a consequence of similar constitution of the most characteristic part of the microbe cell: the living protoplasm.

ORLA-JENSEN has taken these considerations carefully into account when conceiving his natural system of bacteria.

Apart from this, it may be stated that certain natural groups of bacteria, such as those of the true lactic acid bacteria (ORLA-JENSEN's „Lactic acid bacteria“<sup>2)</sup>), those of the colibacteria, in the widest sense (BEIJERINCK's genus *Aerobacter*)<sup>3)</sup>, those of the butyric acid and butyl alcohol bacteria (BEIJERINCK's genus *Granulobacter*)<sup>4)</sup> have become centra in the natural system for many microbiologists.

The system, drawn up recently by a committee of the „Society of American Bacteriologists“<sup>5)</sup> fully takes into account a number of physiological characteristics, but suffers from the evil that the valuation of the more or less essential of the various properties is only slightly successful.<sup>6)</sup>

However one should not imagine that the possibility of classifying all microbes in a limited number of natural groups has become common property of all microbiologists.

As to microbes, which are able to bring about fermentative sugar dissimilation, we will only express the opinion that it is possible to collect practically all these organisms into eight natural groups.

These groups and their characteristic properties are united in table I.

With reference to table I, we wish to mention firstly, that we have given only a few examples in column four, yet we know of no sufficiently

1) S. ORLA-JENSEN, Centralbl. f. Bakteriol. IIe Abt. Bd. 22, p. 305, (1909).

2) S. ORLA-JENSEN, The Lactic Acid Bacteria, Copenhagen (1919).

3) M. W. BEIJERINCK, Centr. f. Bakteriol. IIe Abt. Bd. 6, p. 193, (1900).

4) M. W. BEIJERINCK, Verhandelingen Kon. Ak. van Wetenschappen, Amsterdam, 2nd section Part 1. N<sup>o</sup>. 10 (1893).

5) BERGEY's Manual of Determinative Bacteriology, Baltimore 1923.

6) Compare for example: S. ORLA-JENSEN, Journ. of Bact. Vol. 6, p. 263, (1921).

described sugar fermenting microbes, which cannot be classed in one of the groups given.

Considering this, it may be taken as certainly surprising, that the diversity of sugar fermentative microbes can be reduced to such a small number of groups, which are characterized by relatively so large a number of correlating properties. When directing attention to the products formed in the fermentative decomposition of sugars, at first sight unmistakably a certain connection appears between the nature of the most important products from a quantitative point of view, and the classification into groups on the remaining properties. For instance in table I one finds lactic acid mentioned among the dissimilation products only in groups II, III, IV and V, 2:3 butylene glycol exclusively in groups IV, V, VI, while butyric acid, butyl alcohol and acetone are products which are limited to groups VI, VII and VIII.

On the other hand we must mention that the sugar decomposition products, which are formed by different microbes of one group, in some cases show great differences both from qualitative and quantitative standpoints.

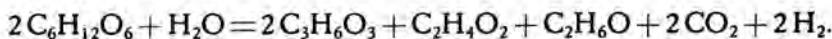
This might give cause to doubt the correctness of the view which we expressed above, that the relationship of microbes is also portrayed in their metabolism.

A closer study of the chemistry of the fermentative sugar dissimilation of different microbes will however show that the differences in dissimilation of microbes belonging to the same group are in no wise of an essential character.

### § 3. *General considerations on the chemistry of the fermentation processes.*

Ever since a beginning was made with the closer study of fermentation processes, attempts to obtain a better idea of the chemistry of these decompositions have been made.

At first one has tried to represent the change brought about by one definite organism in a single chemical equation. As an example we mention only the equation originally given by HARDEN <sup>1)</sup> for the fermentation of glucose by *B. coli*:

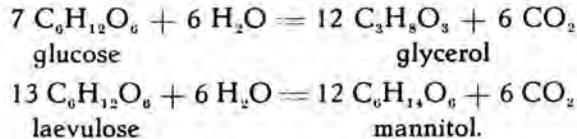


Such a simple equation however is not satisfying, for the simple reason that the quantities of the fermentation products often show variations as the results of modification in the external conditions.

This fact has led some investigators to a mode of explanation in which it is assumed that each of the fermentative products is formed by an independent reaction of the sugar. In those cases where carbon dioxide and hydrogen are produced during fermentation, it is of course easy to write

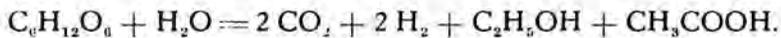
<sup>1)</sup> A. HARDEN, Journ. Chem. Soc. Vol. 79, p. 612, (1901).

down a simple equation, in which a definite fermentation product is derived from the sugar molecule <sup>1)</sup> with the liberation of both gases mentioned. On the other hand it is obvious to what untenable consequences such an opinion leads for those fermentation processes, in which no free hydrogen is formed. BAUMGÄRTEL f.i., in order to explain in this way the occurrence of such products as glycerol and mannitol respectively in lactic acid fermentation has recourse to equations like: <sup>2)</sup>



Between these two extreme opinions stands the explanation according to which a number of more or less independent reactions occur in the fermentation process. According to this supposition the fermentation products will owe their origin, partly to equally and partly to differently directed transformations.

One of the few examples worked out, is found in the study of GREY <sup>3)</sup> on glucose fermentation by means of *B. coli*. In this case the formation of lactic acid was considered to be a distinctly separate process from the formation of the other products, which would be produced from the glucose molecule according to the equation :



In an number of cases GREY was able to explain in a satisfactory way the results obtained, in others however he was not successful. This caused him to abandon his scheme <sup>4)</sup>.

Although undoubtedly the last considered general idea on the chemistry of fermentation processes is correct, it must nevertheless be stated that its application so far has borne but little fruit.

#### § 4. *The fermentative decomposition of sugar in the light of NEUBERG's investigations.*

A new light has been thrown on the chemistry of the fermentative decomposition of sugar <sup>5)</sup> by the researches during the last 14 years of NEUBERG

<sup>1)</sup> Examples of this may be found, among others, in A. KIROW, Untersuchungen zur Buttersäuregärung, Reference Centralbl. f. Bakt. IIe Abt. Bd. 31, p. 534, (1912).

<sup>2)</sup> T. BAUMGÄRTEL, Grundriss der theoretischen Bakteriologie, Berlin (1924).

<sup>3)</sup> E. C. GREY, Proc. Royal Soc. Ser. B., Vol. 87, p. 472, (1914).

<sup>4)</sup> E. C. GREY, *ibid.* Vol. 90, p. 92, (1919).

<sup>5)</sup> Compare the most recent summary in this domain: A. HARDEN, Alcoholic fermentation, 3rd. Edition, London 1923, in which one may find an almost complete list of Neuberg's communications.

and his collaborators. Their first investigations carried out on alcoholic fermentation made it highly probable that the ethyl alcohol produced originated from intermediately formed acetaldehyde<sup>1)</sup>.

In later years followed a series of researches on the fermentative decomposition of sugar under the influence of various bacteria, from which it appeared, that in all probability in these cases acetaldehyde also occurred as an intermediate product. By letting the fermentation take place in the presence of sodium or calcium sulphite or of "dimedon", they succeeded in establishing the formation of acetaldehyde addition products of the above substances.

Apart from alcoholic fermentation they proved this to be the case, for the fermentation of sugar by *B. coli commune*, *B. lactis aerogenes*, *B. dysenteriae*, "Gasbrandbacillus", *Bac. butylicus* Fitz and *Bac. butyricus* Fitz<sup>2)</sup>.

Later on PETERSON and FRED were able to prove in the same way the formation of acetaldehyde by a bacterium of the coli group, by *Bac. acetothylicum* and by *Lactobacillus pentoaceticus*<sup>3)</sup>.

There is no doubt that these observations, which are to a great extent due to the initiative and intelligence of NEUBERG, are of fundamental significance for our insight into the fermentation processes. These researches have made it highly probable that the different fermentation processes of sugar primarily take the same course and that the observed variety in the final products are caused by differences in secondary transformations.

Yet it would appear to us that until now NEUBERG has not derived the full benefit of these important observations.

It is far from our mind to minimise the great significance of the fact that NEUBERG has succeeded in giving a detailed representation of the intermediate changes taking place in the alcoholic fermentation of sugar, which not only explains in an unconstrained way the occurrence of the normal fermentation products but also gives an explanation of the deviations in the course of fermentation in the presence of sulphites and of alkalies respectively (the so called 2nd and 3rd form of fermentation)<sup>4)</sup>.

Still less do we overlook the fact that the observations made by NEUBERG on fermentations brought about by bacteria have given a securer basis to the hypotheses formulated by earlier workers on the origin of definite products

1) KOSTYTSCHEW was the first one who showed acetaldehyde to be an intermediate product in the alcoholic fermentation of sugars. See: Zeitschr. f. physiol. Chemie, Bd. 79, p. 130, (1912); *ibid.* Bd. 79, p. 359, (1912).

2) C. NEUBERG and F. F. NORD, *Bioch. Zeitschr.* Bd. 96, p. 133, (1919);

C. NEUBERG, F. F. NORD and E. WOLFF, *ibid.* Bd. 112, p. 144, (1920);

C. NEUBERG and B. ARINSTEIN, *ibid.* Bd. 117, p. 269, (1921).

H. KUMAGAWA, *ibid.* Bd. 131, p. 157, (1922). The honour is due to GREY for being the first to show in 1913 the occurrence of acetaldehyde in the fermentation of sugar by means of a bacterium (*B. coli*). *Biochem. Journ.* Vol. 7, p. 359, (1913).

3) W. H. PETERSON and E. B. FRED, *Journ. of Biol. Chem.*, Vol. 44, p. 29, (1920).

4) Compare f.i. the summary of W. FUCHS, *Der gegenwärtige Stand des Gärungsproblems*, Stuttgart 1922.

in these fermentation processes. F.i. the demonstration of acetaldehyde as an intermediate product in the dissimilation of sugar has certainly given strong support to the idea already expressed by FITZ <sup>1)</sup> HARDEN <sup>2)</sup>, GREY <sup>3)</sup>, BUCHNER and MEISENHEIMER <sup>4)</sup> that this substance should be a link in the formation of such fermentation products as butylene glycol, butyric acid, butyl alcohol and ethyl alcohol.

It is equally acceptable, as NEUBERG postulated in the 3rd form of alcoholic fermentation, that acetic acid formed in bacterial fermentation owes its formation to a Cannizzaro transformation of acetaldehyde, especially when it is accompanied by at least an equivalent quantity of alcohol.

But all this does not remove the fact that NEUBERG has not yet succeeded in designing a complete scheme for any fermentation brought about by bacteria. Taking into consideration that with nearly all bacterial fermentations, certainly several, simultaneous independent reactions occur, one cannot require of such a scheme, that it will enable to predict the quantities of all the products formed in the fermentation. On the contrary, in designing a fermentation scheme one must take into consideration the fact, that as a consequence of different cultural conditions the various fermentation products likewise occur in varying quantities.

Yet such a scheme should enable to prophesy the consequences of the increase of one of the fermentation products on the quantities of the others.

In so far as, according to the scheme, the origin of two products is directly connected, one ought to find that an increase of one product goes parallel with a similar increase of the other product. Conversely, when certain products owe their origin to the same intermediate product, but are generated from it by independent reactions, one must observe that an increase of one product goes parallel with an equivalent decrease of other products.

A satisfactory scheme for fermentation should further fulfil the requirement, that with its help, one will be able to predict to a certain extent, the result of interfering in an artificial way with the equilibrium of the reactions.

#### § 5. *General scheme for the fermentative decompositions of sugar, brought about by microbes.*

Supporting ourselves on the opinion expressed by NEUBERG, mentioned above, that primarily the same change lies at the basis of the different types of decomposition of sugar and especially under the strain of our conviction, that the relationship of microbe groups will express itself also in the kind

<sup>1)</sup> A. FITZ, Ber. Bd. 13, p. 1309, (1880).

<sup>2)</sup> A. HARDEN and D. NORRIS, Proc. Royal Soc., Ser. B., Vol. 84, p. 492, (1912).

<sup>3)</sup> E. C. GREY, *ibid.* Vol. 87, p. 472, (1914).

<sup>4)</sup> E. BUCHNER and J. MEISENHEIMER, Ber. Bd. 41, p. 1410, (1908).

of dissimilation reactions occurring, we have proceeded to draw up a scheme, which in our opinion, is able to give a picture of the whole domain of the fermentative decomposition of sugar and which fulfils in particular the above formulated requirements.

The scope of this study prohibits us, from entering into a detailed exposition of the arguments, which point in favour of the partial transformations, which lie at the basis of our scheme. It can only be pointed out that in the numerous former researches on one definite type of sugar fermentation experimental proofs are to be found to a large extent. We intend to give a detailed account elsewhere.

Our new scheme is given in Table II. (See Table following page).

Table II gives the reactions, which occur when the hexose molecule is decomposed by any fermentation process. Preparatory to discussing the reactions which are typical for the dissimilation of one particular microbe group in our scheme, a few remarks may be useful.

I. *The initial reaction.* We will state here, that we have fallen in with the hypothesis, as is assumed by previous investigators for some types of fermentation, that in all fermentative decompositions of sugar the hexose molecule is first converted into two molecules of an intermediate product of the empirical formula  $C_3H_6O_3$ . The course of this transformation and the composition of this intermediate products, which certainly is not lactic acid, will be left unconsidered here. We shall only express the opinion that in all fermentative decompositions of sugar the intermediate formation of hexose phosphoric acid esters certainly occurs, as has been shown by HARDEN and YOUNG for alcoholic fermentation <sup>1)</sup>, by EMBDEN and LAQUER for the anaerobic decomposition of sugar in animal muscular tissue <sup>2)</sup> and very recently by VIRTANEN for sugar fermentation by true lactic acid bacteria <sup>3)</sup>.

## II. *The transformations of the hypothetical intermediate product.*

As appears from reaction equation IIa, we assume that the labile hypothetical intermediate product can change into the stable isomer: lactic acid. But simultaneously the intermediate product can undergo a second transformation (IIb), in which it is broken up into formic acid and acetaldehyde. The possibility of showing formic acid and (intermediately) acetaldehyde in all fermentations brought about by bacteria, lends this reaction a high degree of probability, which is still further strengthened by a closer consideration of the metabolism of *B. typhosum* <sup>4)</sup> and the "selected

<sup>1)</sup> See A. HARDEN, Alcoholic Fermentation, Chap. III.

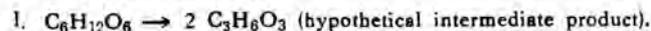
<sup>2)</sup> See for example the summary by O. MEYERHOF, Die Naturwissenschaften, Bd. 12, p. 181, (1924).

<sup>3)</sup> A. I. VIRTANEN, Zeitschr. f. physiol. Chem., Bd. 138, p. 136, (1924).

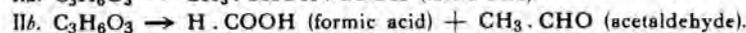
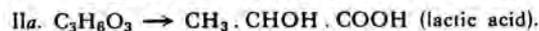
<sup>4)</sup> A. HARDEN, Journ. Chem. Soc., Vol. 79, p. 612, (1901).

TABLE II. GENERAL SCHEME OF THE FERMENTATIVE SUGAR-DISSIMILATION PROCESSES OF MICROBES.

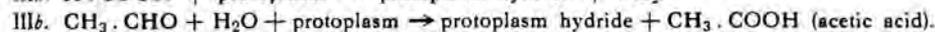
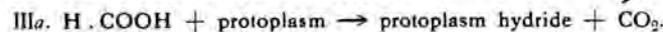
INITIAL REACTION:



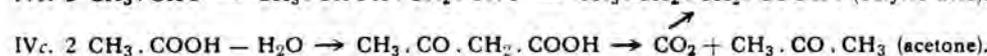
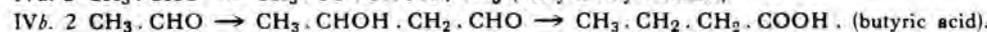
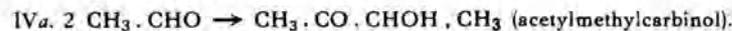
TRANSFORMATIONS OF THE HYPOTHETICAL INTERMEDIATE PRODUCT:



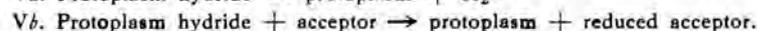
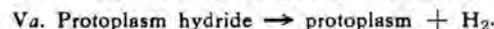
DEHYDROGENATION REACTIONS:



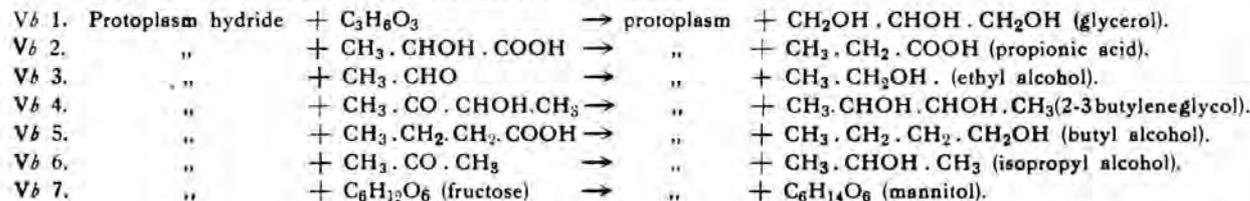
CONDENSATION REACTIONS:



PROTOPLASM REGENERATION REACTIONS:



EXAMPLES OF THE PROTOPLASM REGENERATION REACTION:

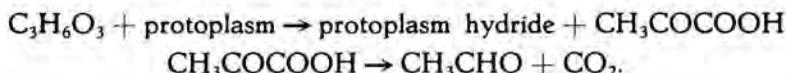


strains" of *B. coli* described by GREY. As regards alcoholic fermentation, it should be remarked that this mode of decomposition of the intermediate product  $C_3H_6O_3$ , put forward in 1906 by SCHADE<sup>2)</sup>, is fairly generally abandoned at present for the change postulated by NEUBERG in which this substance should go over into pyruvic acid. Taking into consideration that

1) E. C. GREY, Proc. Royal Soc. Ser. B., Vol. 87, p. 472. (1914).

2) H. SCHADE, Zeitschr. f. physik. Chemie, Bd. 57, p. 1. (1906).

pyruvic acid has not yet been demonstrated with certainty as an intermediate product in the fermentative decomposition of sugar, — we cannot accept the proof furnished for this view by VON GRAB<sup>1)</sup> nor that of FERNBACH and SCHOEN<sup>2)</sup>. — we find as yet no reason to extend our scheme in this respect. Such an extension would only mean that in alcoholic fermentation the following reactions occur instead of reactions IIb and IIIa :



Since however, both ways lead to the formation of acetaldehyde, hydrogen combined with protoplasm and carbon dioxide<sup>3)</sup>, the choice between the views is of subordinate importance<sup>4)</sup>.

III. *Dehydrogenation reactions.* As a third type of reaction we have assumed that the protoplasm of the fermenting microbes has the property of oxidising various substances by removing hydrogen.

As is well known WIELAND has worked out a theory<sup>5)</sup> according to which the majority of all oxidations can be reduced to a removal of hydrogen from the oxidation substrate, either preceded or not by a preliminary hydration. A powerful experimental support for this theory is undoubtedly the fact that WIELAND has succeeded in causing acetaldehyde to pass over into acetic acid and gaseous hydrogen in the presence of inorganic catalysts, (our reaction IIIb)<sup>6)</sup>.

WIELAND has pointed out repeatedly the advantages which his assumption offers in the explanation of the chemistry of oxidative dissimilation processes. The possibility of extending his considerations to definite reactions in fermentative metabolism has been indicated here and there in his papers, but a thorough development of this idea, as far as we know, has not yet been given.

In our scheme we have limited ourselves to the insertion of two dehydrogenation reactions, namely of formic acid and acetaldehyde. Meanwhile it should be pointed out that the small quantities of succinic acid formed in some fermentations can at least partly owe their existence to the reaction which

<sup>1)</sup> M. VON GRAB, Bioch. Zeitschr. Bd. 123, p. 69, (1921).

<sup>2)</sup> A. FERNBACH and M. SCHOEN, Comp. rend. T. 157, p. 1478, (1913); *ibid.* T. 158, p. 1719, (1914); *ibid.* T. 170, p. 764, (1920).

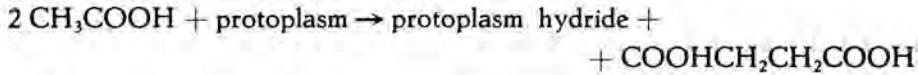
<sup>3)</sup> Cf. S. KOSTYTSCHEW, Die Pflanzenatmung, Berlin, 1924, p. 130.

<sup>4)</sup> A continuation of this study has caused us in the mean time to find extension desirable. We shall return to this elsewhere.

<sup>5)</sup> See: H. WIELAND, Ergebnisse der Physiologie, Bd. 20, p. 477, (1922); *item* Ber. Bd. 55, p. 3639, (1922) and also WIELAND's summary in OPPENHEIMER's „Handbuch der Biochemie“ 2te Aufl., Jena, 1923 Bd. II, p. 252.

<sup>6)</sup> H. WIELAND, Ber. Bd. 46, p. 3327 (1913) and *idem*, Annalen der Chemie, Bd. 431, p. 301, (1923).

THUNBERG has made probable for oxidative metabolism in muscular tissue :



To the possibility of the hypothetical intermediate product undergoing dehydrogenation directly in alcoholic fermentation with the formation of pyruvic acid, we have referred above.

IV. *Condensation reactions.* As regards the reactions under this heading, we wish to remark that reaction IVa has been proved experimentally by the investigations of HARDEN<sup>1)</sup> and those of NEUBERG<sup>2)</sup>. The second type of acetaldehyde condensation is also supported by experiment<sup>3)</sup>. Reaction IVc is made sufficiently acceptable by the fact that production of acetone by suitable microbes is increased with practically the theoretical quantity by the addition of acetic acid during the fermentation process<sup>4)</sup>.

V. *Protoplasm regeneration reactions.* The protoplasm hydrogen compound formed in the reactions described under III, is for different groups of microbes a more or less labile compound. If this compound is more labile it is able to decompose spontaneously into the original protoplasm and gaseous hydrogen (reaction Va). In the case of the more stable protoplasm hydride reformation of protoplasm is only possible by transferring the hydrogen to hydrogen acceptors present simultaneously (reaction Vb). The presence of the ability of a definite kind of protoplasm to give rise to reaction Va nowise excludes reactions of type Vb from taking place at the same time.

Reaction Va finds sufficient support in the occurrence of gaseous hydrogen in many fermentation processes. Reactions Vb, which can occur in the normal dissimilation of sugar, become highly acceptable by the fact on the one hand, that all the products formed are met with among the end products of various decompositions of sugar and on the other hand by the circumstance, that exclusively those substances occur as acceptors, the presence of which in the fermenting medium, be it as substrate (laevulose) or as intermediate product, follows from the preceding reactions.

Meanwhile we wish to state definitely that other substances can also occur as hydrogen acceptors when these are present simultaneously. In this respect we refer to the "phytochemische Reduktionen" carried out by NEUBERG in alcoholic fermentation, which are in no wise limited to this type of fermentation.

<sup>1)</sup> A. HARDEN and D. NORRIS, Proc. Royal Soc., Ser. B., Vol. 84, p. 492, (1912).

<sup>2)</sup> C. NEUBERG and E. REINFURTH, Bioch. Zeitschr. Bd. 143, p. 553, (1923).

<sup>3)</sup> See among several: C. NEUBERG, Bioch. Zeitschr. Bd. 43, p. 491, (1912).

<sup>4)</sup> REILLY and others, Bioch. Journal, Vol. 14, p. 229, (1920); see also: English Patent N<sup>o</sup>. 128403, (1919).

At this stage attention may be drawn to some points which can be deduced from our mode of consideration and which, in their turn are suited to demonstrate the correctness of our ideas regarding the course of fermentative dissimilation.

In the first place we wish to remark that our scheme fulfils the requirement, that it is possible to obtain an insight into the consequences, which arise from an increase in the quantity of one definite fermentation product on the quantities of the other fermentation products. It is obvious, that the prominent occurrence of reaction IIa, i.e. the formation of lactic acid, must go parallel with a corresponding decrease of all changes, which are based on a IIb-reaction. A further consequence of the scheme which follows from reaction IIb is that the formic acid and the products formed from it (carbon dioxide and hydrogen) on the one hand and the acetaldehyde and the products formed from it by secondary reactions on the other, must occur in equivalent quantities, when all is calculated as grammolecules of the two mentioned starting products.

Our scheme contains further another specific requirement, which is also amenable to verification, i.e. that for the protoplasm hydride formation, an equivalent protoplasm regeneration must always take place. This includes that a quantity of hydrogen be it as gas or be it taken up by one or more of the acceptors (Vb-reaction), must be found which is equivalent to the quantity of carbon dioxide and acetic acid<sup>1)</sup> from equations IIIa and IIIb.

Making use of the quantitative results of fermentation found in literature and partly of fermentation balances determined experimentally by ourselves for various types of fermentative sugar dissimilation, it is now possible to test the correctness of the considerations given above. However, as this would lead us too far, we shall be satisfied here with the communication that, taking into consideration the great experimental difficulties, which are encountered in the quantitative determination of some fermentation products, the results obtained answer to the requirements of the scheme in a very satisfactory manner. We intend to elucidate this in more detail elsewhere.

But not only in this particular point do we see a confirmation of the correctness of our views. We will not neglect to emphasise here how the idea of WIELAND concerning the dehydrogenations and hydrogenations taking place under the influence of protoplasm, applied in this scheme, offers great advantages over the more general explanation of the phenomenon of oxidation and reduction processes occurring in the course of fermentation. Following NEUBERG's example these processes are fairly generally explained by the introduction of the well known Cannizzaro transformation.

Meanwhile it is in no way possible to explain with the aid of these trans-

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<sup>1)</sup> Taking into account also the separate formation of carbon dioxide and disappearance of acetic acid in those cases where acetone and (or) isopropyl alcohol occur as fermentation products.

formations, which are always limited to aldehydes, the formation of a number of the products normally occurring in fermentations and obviously formed by reduction. We need only mention propionic acid, isopropyl alcohol, 2 : 3 butylene glycol, mannitol, etc.

Also the explanation of the occurrence of acetic acid in the fermentative decomposition of sugar, by means of a simple or mixed Cannizzaro transformation of acetaldehyde cannot in general be sustained, as in that case a quantity of monohydric or polyhydric alcohols equivalent to the acetic acid must always be formed. In the fermentation of sugar by true butyric acid bacteria considerable quantities of acetic acid are produced without alcohols occurring simultaneously. We proved the reduction-equivalent apparently missing to be free hydrogen <sup>1)</sup>.

Not only does our scheme give an unconstrained explanation for all these facts but also it is excellently suited to throw a clear light on the unmistakable connection, which exists between the normal fermentation phenomena and the reducing powers of liquids in fermentation towards very diverse substances. In so far as the reduction of added aldehyde is concerned one can always keep to the explanation of a mixed Cannizzaro reaction of NEUBERG. But this explanation completely fails us in those cases, in which substances such as nitrobenzene, molybdenic acid, vanadic acid, methylene blue and sulphur are reduced. Everything is completely intelligible in the train of thought associated with our scheme since the substances mentioned simply act as hydrogen acceptors in reaction Vb.

On the basis of these facts it is evident that there exists no reason whatever to have recourse in certain cases to the narrower explanation afforded by a CANNIZZARO transformation.

The representation of the chemistry of the reduction and oxidation phenomena put forward gives at the same time means of explaining the connection, which undoubtedly exists between the chemistry of dissimilation and that of assimilation.

In this connection we will remind to the well known researches of FELIX EHRLICH on the primary reactions which  $\alpha$ -amino-acids undergo in assimilation by alcohol yeast <sup>2)</sup>. Nowadays the idea is fairly generally assumed that the first reaction of these  $\alpha$ -amino-acids is an oxidation to the corresponding  $\alpha$ -keto-acids with the splitting off of ammonia <sup>3)</sup>. These in their turn are decomposed into carbon dioxide and the corresponding aldehydes, which are converted subsequently into the corresponding alcohols (the alcohols of fusel oil) by reduction and the corresponding acids by oxidation. The conversion of glutamic acid into succinic acid is the best known example of the latter change.

<sup>1)</sup> An investigation of one of us not yet published (D.).

<sup>2)</sup> A list of EHRLICH's communications can be found in A. HARDEN, *Alcoholic Fermentation*, loc. cit.

<sup>3)</sup> O. NEUBAUER and K. FROMHERZ, *Zeitschr. f. physiol. Chem.* Bd. 70, p. 326, (1911); See also A. HARDEN, *Alcoholic Fermentation*, p. 137.

It is certainly important that these reactions completely fit into the spirit of the scheme. We need only add to this scheme a most obvious extension and assume that the protoplasm will exert its dehydrogenating action on the substrates of assimilatory metabolism and the primary oxidation of amino-acids to keto-acids appears as a self evident fact.

The reduction of the aldehydes to alcohols falls in completely with reactions Vb, just as was remarked above for the „phytochemische Reduktionen“. Finally, the sometimes continued oxidation of the aldehydes formed is completely comprehensible by the assumption of a further extension of the dehydrogenation reactions.

Still this is not all which can be put forward in favour of our views regarding the course of fermentation reactions.

Above we placed the requirement on a satisfactory scheme that by its aid one should be able to a certain degree to predict the result of artificial interference with the equilibrium of the reactions.

Owing to lack of space we shall not consider in particular, which predictions may be given for the various types of dissimilation on the basis of our scheme. We will be satisfied by stating that on the basis of many considerations taken from the scheme, we have come to the conclusion that by choosing suitable conditions it ought to be possible to bring about the fermentative production of acetyl-methyl-carbinol and 2 : 3 butylene glycol from *sugars* by means of yeast and representatives of the group of true lactic acid bacteria. As appears from our second paper, which immediately follows this, the results have completely confirmed our expectations.

§ 6. *The relationship of microbes expresses itself also in the fermentative decomposition of sugars.*

As already observed in the preceding paragraph we have considered for various microbes belonging to diverse groups in how far the observed results of fermentation answer to the requirements of the scheme put forward.

The limited available quantitative data naturally make it impossible to extend this investigation to all the kinds of sugar-fermentative microbes so far described.

But we can still see in how far the scheme is able to explain the qualitative results of all cases of the fermentative decomposition of sugar, which are sufficiently described, by the occurrence of a particular combination of partial reactions from the scheme. And the question naturally follows in how far the relationship of microbes from the same natural group expresses itself in the combinations of reactions to which their mode of fermentation may be reduced.

It suffices here to give in Table III, which combination of partial reactions is encountered with each of the species of microbes. We have limited

TABLE III. SUMMARY OF THE FERMENTATIVE DISSIMILATION OF SUGAR FOR THE VARIOUS GROUPS.

		GROUP I	GROUP II		GROUP III	GROUP IV			GROUP VI		GROUP VII	
		Alcohol yeasts	Homofermentative lactic acid bacteria	Heterofermentative lactic acid bacteria	True propionic acid bacteria	Sub-group of <i>B. typhosum</i>	Sub-group of <i>B. coli</i>	Sub-group of <i>B. aerogenes</i>	Sub-group of <i>Bac. polymyxa</i>	Sub-group of <i>Bac. macerans</i>	True butyl alcohol bacteria	True butyric acid bacteria
Initial reaction	I	+	+	+	+	+	+	+	+	+	+	+
Reactions of the hypothetical intermediate product	IIa	-	+	+	+	+	+	+	+	+	+	+
	IIb	+	-	+	+	+	+	+	+	+	+	+
Dehydrogenation reactions	IIIa	+	.	+	+	- <sup>⊕</sup>	+ <sup>⊖</sup>	+	+	+	+	+
	IIIb	- <sup>⊕</sup>	.	+	+	+	+	+	+	+	+	+
Condensation reactions	IVa	- <sup>⊕</sup>	.	- <sup>⊕</sup>	-	-	- <sup>⊕</sup>	+	+	+	+	+
	IVb	- <sup>⊕</sup>	.	-	-	-	-	+	+	+	+	+
	IVc	-	.	-	-	-	-	+	+	+	+	-
Protoplasm regeneration reactions	Va	-	.	+	-	-	+ <sup>⊕</sup>	+	+	+	+	+
	Vb	+	.	+	+	+	+	+	+	+	+	- <sup>⊕</sup>
Predominant protoplasm regeneration reactions	Vb 1	+	.	+	.	.	.	.	.	.	.	.
	Vb 2	.	.	.	+	.	.	.	.	.	.	.
	Vb 3	+	.	+	.	+	+	+	+	+	.	.
	Vb 4	.	.	.	.	.	.	+	+	.	.	.
	Vb 5	.	.	.	.	.	.	.	+	.	+	.
	Vb 6	.	.	+	.	.	.	.	.	.	+	.
	Vb 7	.	.	+	.	.	.	.	.	.	.	.

ourselves to one statement as far as these reactions are identical for various species of microbes belonging to one and the same group.

Groups V and VIII are not included in the table, because the types of sugar dissimilation of these groups are completely covered by those of groups IV and VII.

The table requires but little further explanation. We need only remark that the sign + indicates that for the particular microbes the corresponding reaction occurs in the normal fermentation of sugar; the sign — shows that the reaction does not take place; the sign  $\oplus$  that a reaction not occurring under normal conditions can be realised under special conditions, while the sign  $\ominus$  indicates that it is possible to cause a normally occurring reaction to disappear whilst retaining the remaining partial reactions.

Perusing this table, in the first place it may be taken as highly satisfactory that only a limited number of dissimilation types are encountered in each of the groups. Apart from any other consideration it need not be excluded that all the eleven differentiated types of dissimilation, should occur in each of the groups, which have been set up chiefly on the basis of other properties. In the fact that this is not the case we see a proof of our conviction expressed in § 2, that the relationship of microbes will be reflected in the kind of the dissimilation reactions. And this proof is still strengthened by a closer study of the different types of dissimilation met with in one and the same group, as it appears that the difference in one group can be practically always explained by the occurrence or non-occurrence of one single partial reaction, which then in certain cases carries with it the occurrence or absence of further secondary reactions.

For instance the difference between the homofermentative and heterofermentative lactic acid bacteria <sup>1)</sup> finds its explanation in the absence of reaction IIb with the former.

The large agreement in the dissimilation reactions in the sub-group of *B. typhosum* and that of *B. coli* is obvious from the fact that GREY was able to obtain the so called "selected strains" by cultivating *B. coli* on media containing chloroacetates, the dissimilation of which strains was a picture of that of *B. typhosum*.

The difference between the subgroup of *B. coli* and that of *B. aerogenes* lies exclusively in the presence of the acetylmethylcarbinol condensation and the in consequence occurring prevalence of an other reduction reaction (Vb 4) in the latter group.

The difference between the subgroup of *Bac. polymyxa* and that of *Bac. macerans*, according to the table is exclusively due to the presence of the IVb condensation in the former. Meanwhile this condensation occurs to

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<sup>1)</sup> We introduce this nomenclature for the first time for describing the difference long known to the fermentation and dairy microbiologists between the true lactic acid bacteria which form exclusively lactic acid and those which also form volatile acids, alcohol and carbon dioxide.

such a small extent that it is justified to raise the question if there is sufficient reason for drawing up the subgroups. Nevertheless we decided to this differentiation because with the former the carbinol condensation and with the latter the acetylacetic acid condensation is so strongly pronounced.

Further, the difference between true butyric acid and true butyl alcohol bacteria may be ascribed to the fact that in the former the protoplasm hydride is more labile than in the latter, with the consequence that practically all hydrogen acceptor reactions remain absent.

Finally we will point out that for groups which from the data in the third column of Table I possess a closer relationship, this also holds true for the corresponding types of sugar dissimilation. Meanwhile we do not wish to conclude that similarity in type of sugar dissimilation, or more broadly: similarity in metabolism, always means a close relationship. It must never be lost sight of, that at one time or another in more or less independent phylogenetic series similar metabolism processes can occur.

*Delft*, November 1924.

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**Microbiology.** — A. J. KLUYVER and H. J. L. DONKER: "*The formation of acetylmethylcarbinol and 2 : 3 butylene glycol in the fermentation of sugars by alcohol yeasts and true lactic acid bacteria.*" (Communicated by Prof. G. VAN ITERSON JR.)

(Communicated at the meeting of November 29, 1924).

The formation of 2 : 3 butylene glycol and acetylmethylcarbinol in the fermentative decomposition of sugar under the influence of microbes was first demonstrated by HARDEN and WALPOLE in 1908<sup>1)</sup>. These investigators found that in the fermentation of sugar under the influence of *B. lactis aerogenes*, the glycol, together with small quantities of acetylmethylcarbinol, was present among the fermentation products to the extent of 20 percent of the weight of sugar fermented.

The mode of production of these two compounds was explained in 1912 by HARDEN and NORRIS<sup>2)</sup> by the assumption of a condensation of immediately formed acetaldehyde.

In later years, a series of communications by LEMOIGNE<sup>3)</sup> has shown the occurrence of both the substances mentioned in the metabolism of very diverse microbes. Among these one finds both organisms, which possess exclusively an oxidative dissimilation and also those, which are able to bring about the splitting of sugars by fermentation. While we shall omit of consideration here the formation of acetylmethylcarbinol by the first mentioned organisms, we shall first consider to which of the groups given in the preceding communication<sup>4)</sup>, the sugar fermenting microbes, which have been shown to produce these compounds, belong. It appears that all these microbes belong to groups IV and V. To this might be added immediately, that unpublished investigations, which we have carried out, have taught us that the products mentioned are also encountered very frequently among the normal fermentation products of microbes belonging to groups VI and VII. On the contrary these substances have not been found so far in the normal fermentative decomposition of sugar by microbes of groups I, II and III.

As will appear quite clearly from what is given below, this contrast is connected in a close manner with the fact, that free hydrogen is completely

1) HARDEN and G. S. WALPOLE, Proc. Royal Soc. Ser. B. Vol. 77, p. 399, (1906).

2) A. HARDEN and D. NORRIS, Proc. Royal Soc. Ser. B. Vol. 84, p. 492, (1912).

3) M. LEMOIGNE, Annales de l'Institut Pasteur T. 27, p. 856, (1913); Comp. rend. de la Soc. de Biol. T. 82, p. 984, (1919); Ibid. T. 83, p. 336, (1920); Comp. rend. de l'Acad. d. Sc. T. 177, p. 652, (1923); Compt. rend. de la Soc. de Biol. T. 88, p. 467, (1923).

4) These Proceedings 28, p. 297 (1925).

or almost completely absent among the fermentation products of the last mentioned groups of microbes.

A short time ago it was shown by NEUBERG and REINFÜRTH<sup>1)</sup>, however, that if acetaldehyde is added to a sugar solution undergoing fermentation by brewer's yeast or pressed yeast, the acetaldehyde added is converted almost quantitatively into acetylmethylcarbinol. The fact that the product so formed appears to be optically active leaves no doubt as regards the biochemical character of the condensation which occurs. In this condensation NEUBERG sees a special case of the carbon coupling action of yeast, which he has established with a number of other aldehydes and which should take place under the influence of what he describes as a carboligase enzyme.

No further proof is necessary that this carboligatic action on added acetaldehyde is precisely the same as the condensation, which has already been recognised by HARDEN as the cause of the occurrence of acetylmethylcarbinol (and indirectly of 2 : 3 butylene glycol) in the normal fermentation of sugar by *B. lactis aerogenes*.

While on the one side, from the researches of NEUBERG and REINFÜRTH it appears that alcohol yeast is able to bring about the carbinol condensation of acetaldehyde and on the other side it is established that acetaldehyde is an intermediate product in the normal fermentation of sugar by this organism, the question naturally presents itself, why carbinol, or its reduction product 2 : 3 butylene glycol, is not formed in the normal fermentation, as has also been stated by NEUBERG.

The only plausible explanation for this fact is, that the acetaldehyde formed intermediately undergoes other transformations so rapidly, that it is withdrawn from the simultaneously possible carbinol condensation.

The scheme, which we have developed for alcoholic fermentation and which may be gathered from Tables II and III of our preceding communication, clearly indicates that it is the protoplasm-hydrogen compound, which makes itself master of the acetaldehyde. Indeed, where protoplasm regeneration with the liberating of free hydrogen by the yeast cannot take place, the re-formation of protoplasm is left completely to the collaboration of a hydrogen acceptor, the acetaldehyde then functioning as such.

If this view is correct, then interference with the metabolism, the direct consequence of which is the introduction at least partially of another protoplasm regeneration reaction, must result in an excess of acetaldehyde in first instance. Now where acetaldehyde added externally is converted by yeast into acetylmethylcarbinol, one might expect that the method of interference, described above, will lead in like manner to the production of the carbinol or to its reduction product 2 : 3 butylene glycol.

In this line of thought we have investigated the result of the addition of hydrogen acceptors on the course of the normal fermentation of sugar.

<sup>1)</sup> Bioch. Zeitschr. Bd. 143, p. 553, (1923).

In complete agreement with expectation it appears, that if a ten percent glucose solution, to which 0.1 percent of methylene blue or a few percent of sulphur has been added, is allowed to ferment at a temperature of 30° C. by means of 10 percent pressed yeast (Koningsgist der Ned. Gist- en Spiritus-fabriek, Delft) with the exclusion of air, the formation of 2 : 3 butylene glycol can be demonstrated with certainty in the completely fermented liquid within three hours. It is wellnigh superfluous to remark, that the added methylene blue was completely reduced to the leuco-compound, while in the other experiments the added sulphur was converted into hydrogen sulphide to a noticeable extent.

In these and all subsequent experiments the presence of acetylmethylcarbinol or 2 : 3 butylene glycol respectively, was demonstrated by the excellent method of LEMOIGNE<sup>1)</sup>, in which first the carbinol present is converted into diacetyl by oxidation with ferric chloride and afterwards any glycol is oxidised by bromine<sup>2)</sup> in neutral solution to diacetyl also, the latter being indentified by steam distillation into an ammoniacal solution of nickel chloride and hydroxylamine, as the highly characteristic nickel dimethylglyoxime.

This confirmation of our expectations led us to the suggestion, that probably also with the heterofermentative, true lactic acid bacteria the absence of carbinol and glycol among the normal products of glucose fermentation — concerning which we especially reassured ourselves — must be ascribed neither to a lack of power to form carbinol. We found it to be possible to force the production of carbinol in sugar fermentation, in the same way as given above for alcoholic fermentation, for a couple of representatives of this groups, namely, *Lactobacillus fermentum* (BEIJERINCK) and *Betabacterium breve* (ORLA-JENSEN). As it is not possible to start with a large quantity of bacteria material, one must choose the added hydrogen acceptor for these bacteria in such a way, that there is no retarding influence on the growth. As appears from our scheme, laevulose is pre-eminently suitable for bacteria of the group mentioned, to serve both as dissimilation substratum and hydrogen acceptor. In a sterile culture liquid, consisting of yeast extract with 10 percent of laevulose, inoculated with one of the bacteria strains after incubating for several days (at 30°—35° C. for *L. fermentum* and at 25° C. for *B. breve*.) 2 : 3 butylene glycol could be demonstrated.

The positive results of these experiments opened up the possibility of investigating in this way whether, be it in a very small degree, laevulose also acts as a hydrogen acceptor in alcoholic fermentation.

As a matter of fact we found that 2 : 3 butylene glycol (together with

<sup>1)</sup> M. LEMOIGNE, Annales de l'Institut Pasteur, T. 27, p. 856, (1913); Compt. rend. T. 170, p. 131, (1920).

<sup>2)</sup> To us it appeared that in this oxidation the presence of ferric chloride as a catalyst is necessary.

some unchanged acetaldehyde) can be shown in the fermentation of a 10 percent solution of laevulose with 10 percent pressed yeast after three hours. Under the same conditions no glycol or carbinol and at most a trace of acetaldehyde appears to be formed in the glucose fermentation.

By fermenting 10 percent laevulose in LEBEDEV's maceration extract prepared from brewer's yeast, the hydrogen acceptor function of the laevulose according to the strong acetylmethylcarbinol reaction, becomes even more prominent, which is in every respect conceivable, on account of the direct contact of the laevulose in high concentration with the fermentative agent. By means of a special control experiment we convinced ourselves that by using glucose instead of laevulose no production of carbinol or glycol took place.

Thus we see how the general scheme for the fermentative decomposition of sugar, which we have put forward, has led to the fact, that in future the formation of acetylmethylcarbinol or 2 : 3 butylene glycol from laevulose under quite normal conditions of fermentation of this sugar by means of alcohol yeast must be taken into account.

*Delft, November 1924.*

**Mathematics.** — “A Representation of the Linear Complex of Rays on the Points of Space”. By Prof. JAN DE VRIES.

(Communicated at the meeting of January 31, 1925).

1. R. STURM (*Liniengeometrie*, I, p. 265) gives a simple derivation of the usual representation (1, 1) of the linear complex of rays  $L$  on space.

In order to arrive at another representation we assume a plane pencil  $(A, a)$  which does not belong to  $L$ , and a point  $M$  outside it. The sheaf round the point  $A'$  chosen at random, is brought into a projective correspondence with the sheaf round  $A$ .

If  $R$  is the point of intersection of  $a$  with the ray  $r$  of the complex,  $\varrho$  the plane  $A'r$ ,  $\varrho'$  the plane through  $A'$  corresponding in the projectivity to  $\varrho$ , we consider the point of intersection  $R'$  of  $\varrho'$  and  $MR$  as the image of the ray  $r$ .

Inversely an arbitrary point  $R'$  corresponds as image to a definite complex-ray. To the pencil of planes  $(\varrho')$  round  $A'R'$  a pencil  $(\varrho)$  is associated. One of its planes passes through the point of intersection  $R$  of  $a$  and  $MR'$ , and its intersection with the null-plane of  $R$  is the ray  $r$  that is represented in  $R'$ .

2. *Singular rays (a).* Let  $N_0$  be the null-point of  $a$ ,  $r_0$  a ray of the plane pencil  $(N_0, a)$ . Any point  $R_0$  of  $r_0$  may be considered as the passage of  $r_0$ . If in the projective sheaves round  $A$  and  $A'$  the plane  $a'$  corresponds to  $a$  and if  $r_0^*$  is the projection of  $r_0$  out of  $M$  on  $a'$ ,  $r_0$  has for image the point-range on  $r_0^*$ . The plane pencil  $(N_0, a)$  consists accordingly of rays which are singular for the representation. The images of its rays form the plane pencil  $(N_0^*, a')$ .

*b.* For a complex-ray  $r$  in the null-plane of  $A$ ,  $R$  lies in  $A$ ; any plane through  $r$  may be considered as a plane  $\varrho$ . The homologous pencil  $(\varrho')$  defines on  $m \equiv MA$  a point-range which represents  $r$ .

This point-range is apparently the image of the whole plane pencil  $(r)$  round  $A$ ; all the rays are singular. But also all the points of  $m$  are singular for the representation and each is an image of  $(r)$ .

*c.* For the ray  $AN_0R$  and  $\varrho$  are both indefinite so that it is represented by the plane pencil projecting it out of  $M$ . It is, therefore, a cardinal ray for the representation.

*d.* A ray  $r$  is also singular if  $MR$  lies in  $\varrho'$ ; in this case  $\varrho'$  contains the line  $k' \equiv MA'$ . The pencil  $(\varrho')$  round  $k'$  is projective with the pencil  $(\varrho)$  round the line  $k$  (passing through  $A$ ).

The hyperboloid produced by them cuts  $\alpha$  in a conic  $\alpha^2$  (through  $A$ ). Through any point  $R$  of  $\alpha^2$  there passes a singular ray  $r$  (the intersection of  $\varrho$  with the null plane of  $R$ ). Through a point  $P$  of  $k$  there pass two rays  $r$  resting on  $\alpha^2$ ; hence  $k$  is a *double directrix* of the scroll of the singular rays. As a plane through  $k$  contains one ray  $r$ , the scroll ( $r$ ) is *cubical*; its other directrix is the polar line of  $k$  relative to  $\mathbf{L}$ .

Each straight line of the scroll ( $r$ )<sup>3</sup> has for *image* the *point-range* ( $R'$ ) on a definite *generatrix*  $MR$  of the *quadratic cone* ( $M, \alpha^2$ ).

3. *Singular points* (a). If we choose  $R'$  in  $A'$ , hence  $R$  in the point of intersection  $A_0$  of  $\alpha$  and  $MA'$ , the rays  $r$  in the null plane of  $A_0$  are projected out of  $A$  by a pencil ( $\varrho$ ) round the axis  $AA_0 \equiv a$ ; the homologous pencil ( $\varrho'$ ) round  $a'$  cuts  $MA_0$  in  $A'$ . Accordingly  $A'$  is a *singular point* and the *image* of the *complex-plane pencil* round  $A_0$ .

b. A plane pencil of  $\mathbf{L}$  which has its vertex on the ray  $r_0 \equiv AN_0$ , is represented by a point  $R'$ , which is accordingly *singular*. If  $R$  describes the point-range on  $r_0$ , its null plane  $\varrho$  revolves round  $r_0$  and  $\varrho'$  describes a pencil that is projective with the point-range ( $R$ ), hence with the plane pencil ( $MR$ ).

Consequently there is a conic  $\alpha^2$  of which each point  $R'$  is the *image* of a *complex-plane pencil* containing  $r_0$ . These plane pencils form the *parabolic congruence* [1, 1] round  $r_0$  as axis.

c. A complex-plane pencil ( $r$ ) containing a ray of the plane pencil ( $N_0, \alpha$ ), is projected out of  $A$  by a pencil ( $\varrho$ ) round the axis  $AR \equiv a$ . If  $R'$  lies on the homologous ray  $a'$ , this point is *singular*, and the *image* of ( $r$ ).

If  $a^*$  is the projection of  $a$  out of  $M$  on  $a'$ , and  $A^*$  the projection of  $A$ , the singular point  $R'$  is the intersection of  $a'$  and  $a^*$ . If  $a$  revolves round  $A$ ,  $R'$  describes accordingly a *conic*  $\alpha_*^2$  which passes through  $A'$  and  $A^*$ . Each of its points is the *image* of a *complex-plane pencil* which contains a ray through  $N_0$ .

Out of  $M \alpha_*^2$  is projected on  $\alpha$  in a conic through the point  $A$  and the passage  $K'$  of  $k'$ . Through  $a'$  there passes a plane  $\varrho'$  which contains  $MR$ ; hence  $R$  is a point of  $\alpha^2$  (§ 2) and  $\alpha^2$  is the projection of  $\alpha_*^2$ .

d.  $M$  is a *cardinal point* of the representation. For if  $R'$  lies in  $M$ ,  $R$  may be any point of  $\alpha$ ,  $\varrho'$  any plane through  $k' \equiv A'M$ , hence  $\varrho$  any plane through  $k$ . The complex-plane pencil in a plane  $\varrho$  is represented in  $M$ .  $M$  is apparently the *image* of the *net of rays* [1,1] in which  $\mathbf{L}$  is cut by the axial complex round the axis  $k$ .

4. *Image of a plane pencil*. The rays  $r$  of a complex-plane pencil ( $N, \nu$ ) define on  $\alpha$  a point-range ( $R$ ) and a pencil of planes ( $\varrho$ ) round  $AN$ . The corresponding pencil ( $\varrho'$ ) is projective with the plane pencil ( $MR$ ). The *image* of the plane pencil is accordingly a *conic*  $\nu^2$  through  $M$ .

If  $N$  lies in  $\alpha$ , all the rays except  $NN_0$  have the same passage  $R \equiv N$ .

In this case the *image* consists of the *straight line*  $MN$  and the *straight line* through  $N_0^*$ , that represents the ray  $N_0N$ .

In particular the plane pencil round  $A$  is represented by the line  $m$  and a line through  $N_0^*$ .

5. *Image of a net of rays.* The rays of  $\mathbf{L}$  resting on the line  $d$ , hence also on the polar line  $d^*$ , form a  $[1, 1]$ . The rays resting moreover on  $k$ , have  $M$  for image; they form a quadratic scroll which cuts  $a$  in a conic  $(R)^2$ . The cone projecting it out of  $M$ , consists of straight lines which touch the image surface of the congruence at  $M$ . As each point  $R$  of  $a$  is the passage of a ray of the  $[1, 1]$ , each straight line  $MR$  contains one point  $R'$  outside  $M$ .

The image is accordingly a *nodal cubic surface*  $O^3$  with a conical point in  $M$ .

$O^3$  contains the conics  $\sigma^2$  and  $\sigma_*^2$ , for each plane pencil that has a point of one of these curves as image, has one ray in the congruence. For the same reason the line  $m$  lies on  $O^3$ .

As  $d$  cuts three rays of the scroll  $(r)^3$ , there pass through  $M$  three straight lines of  $O^3$ , representing complex rays.  $O^3$  also contains the point  $A'$  (image of a ray of the plane pencil round  $A_0$ ), and a straight line through  $N_0^*$  (image of a ray through  $N_0$ ).

6. *Image of a quadratic scroll.* The images of two nets of rays have in common the line  $m$ , the conics  $\sigma^2$  and  $\sigma_*^2$ , and besides a *twisted curve*  $\varrho^4$  with node  $M$ . This is the *image* of the scroll  $(r)^2$  which consists of the common rays of the nets.

We can also arrive at this image in the following way. The image curve of  $(r)^2$  lies on the cone projecting the passage  $(R)^2$  of  $(r)^2$  out of  $M$ . Each generatrix contains one point  $R'$  besides  $M$ . Two rays  $r$  rest on  $k$ ; hence  $M$  is node of the image curve, which is accordingly a  $\varrho^4$ .

7. *Scroll which is represented on a straight line.* The straight line  $g^*$  has three points in common with  $O^3$  (§ 5); consequently there are three points  $R'$  which represent rays  $r$  that rest on  $d$ . The scroll  $(r)$  is *cubical* and has as directrix the projection  $g$  of  $g^*$  out of  $M$  on  $a$ . The polar line of  $g$  relative to  $\mathbf{L}$  is apparently the second (double) directrix.

8. *Congruence which has a field of points as image.* The plane  $\Omega$  of the field  $[R']$  has two points in common with the image of a complex-plane pencil. Accordingly there exists a congruence  $[2, 2]$  which has  $[R']$  as image. This congruence contains the 5 plane pencils which are represented in the points of intersection of  $\Omega$  with  $m$ ,  $\sigma^2$  and  $\sigma_*^2$ .

**Mathematics.** — “A Representation of the Quadratic Complex of Rays on the Points of Space”. By Prof. JAN DE VRIES.

(Communicated at the meeting of January 31, 1925).

Representations (1, 1) of the quadratic complex of rays  $\mathbf{Q}$  have been described by CAPORALI and by MONTESANO <sup>1)</sup>. In the following paper a new representation is treated.

1. Let  $(A, a)$  be a plane pencil of  $\mathbf{Q}$  with rays  $a, A'$  the center of a sheaf which is projective with the sheaf round the point  $A$ , and  $M$  a given point. If  $r$  is a complex ray,  $R$  its passage through  $a, \varrho$  the plane  $A r, \varrho'$  the homologous plane through  $A'$ , we consider the point of intersection  $R'$  of  $\varrho'$  and the line  $M R$  as the *image* of the ray  $r$ .

It appears in the following way that an arbitrary point  $R'$  is the image of a definite ray  $r$ . To the pencil of planes  $(\varrho')$  through the straight line  $l' \equiv A'R'$  there corresponds a pencil  $(\varrho)$  through the homologous line  $l$ . Together with  $a$  the line  $M R'$  defines the point  $R$ ; the plane  $R l$  cuts the complex-cone  $(R)^2$  of  $R$  along  $R A$  and along a second ray  $r$ , and this ray has  $R'$  for image.

2. Every ray  $a$  of  $(A, a)$ , is *singular*, for any of its points may be considered as passage  $R$ . The plane  $\varrho$  corresponding to a point  $R$  must touch the cone  $(R)^2$  along  $a$ . The point-range  $(R)$  is projective with the pencil of planes  $(\varrho)$ , hence with the homologous pencil  $(\varrho')$ , and also with the plane pencil  $(M R)$ . Consequently the locus of the points  $R'$  is a conic  $\varrho_0^2$  through  $M$  which cuts the homologous line  $a'$ . If  $R$  gets into  $A$ ,  $\varrho$  coincides with  $a, \varrho'$  with  $a'$ , and  $R'$  gets into the point of intersection  $M^*$  of  $M A$  with  $a'$ . The *images* of the *singular rays*  $A$  are therefore *conics* through the points  $M$  and  $M^*$ .

Let  $\alpha^*$  be the plane of the second complex-plane pencil that has  $A$  as vertex,  $a^*$  the intersection of  $a$  and  $\alpha^*$ . Any plane through  $a^*$  may be considered as the tangent plane  $\varrho$  at  $A$  to the complex-cone  $(A, \alpha^*)$ . The image of  $a^*$  is accordingly the point-range on the line  $m \equiv M A$ .

The *image* of the *plane pencil*  $(A, a)$  is a *binodal cubic surface*  $\mathbf{A}^3$  which has *conical points* in  $M$  and  $M^*$ .

If  $A^*$  is the vertex of the other complex-plane pencil in  $a$ , the tangent plane  $\varrho$  coincides with  $a$  for each point of the ray  $A A^*$ ; in this case

<sup>1)</sup> Cf. R. STURM, *Liniengeometrie* III, 272 and 395. The representation of MONTESANO deals with a  $\mathbf{Q}$  with two double rays.

the image points  $R'$  lie on the line of intersection  $d$  of  $a'$  and the plane  $MAA^*$ .

3. The rays  $r^*$  of the *plane pencil*  $(A^*, a)$  are also *singular* for the representation. The plane  $\varrho$  coincides with  $a$ ,  $R$  is an arbitrary point of  $r^*$ ; hence  $R'$  is a point of the line of intersection of the planes  $a'$  and  $Mr^*$ .

The image of  $r^*$  is a *point-range*; the *plane pencil*  $(A^*, a)$  is represented on a *plane pencil* of  $a'$ .

Also the rays of the *plane pencil*  $(A, a^*)$  are *singular*, for  $R$  lies in  $A$  and  $\varrho$  is an arbitrary plane through  $r$ . The image of the ray  $r$  is the *point-range* on the line  $m$ .

If the line  $MR$  lies in the plane  $\varrho'$ , the ray  $r$  is represented on the point-range of  $MR$ ; it is, therefore, a *singular ray*. In this case  $\varrho'$  belongs to the pencil of planes through the line  $k' \equiv A'M$ , and  $\varrho$  to the pencil of planes through the homologous line  $k$ . The projective pencils  $(\varrho)$  and  $(\varrho')$  produce a hyperboloid; the *conic*  $a^2$  along which it cuts the plane  $\alpha$ , is the locus of  $R$ . Through each point of  $a^2$  there passes a singular ray,  $s$ ; it rests on  $k$ . A plane through  $k$  contains one ray  $s$ . Through a point of  $k$  there pass the four rays  $s$  of its complex-cone which rest on  $a^2$ .

There is accordingly a *scroll*  $(s)^5$  of *singular rays* each of which has for *image* the *point-range* on one of the generatrices of the cone which projects  $a^2$  out of  $M$ .

4. Any point  $R'$  of  $m$  is *singular* and the image of the *plane pencil*  $(A, a^*)$ .

If  $R'$  lies in  $M$ ,  $R$  is an arbitrary point of  $\alpha$ ,  $\varrho'$  an arbitrary plane through  $k'$ ,  $\varrho$  an arbitrary plane through  $k$ . Each complex-ray in  $\varrho$  has  $M$  for image. Hence  $M$  is a *cardinal point* of the representation and the image of all the rays of the congruence  $[2, 2]$  that rest on  $k$ .

5. There are two more groups of *singular points*  $R'$ ; they were pointed out to me by Dr. G. SCHAAKE.

The complex-rays through a point  $R$  of  $\alpha$  define a pencil of planes  $(\varrho)$  round the axis  $a \equiv AR$ . The homologous planes  $\varrho'$  round the axis  $a'$  (in  $\alpha'$ ) generally define each a point  $R'$ . But if  $a'$  cuts the line  $MR$ , the point of intersection  $R'$  is the image of any ray  $r$  of  $(R)^2$ ; hence it is *singular*. The *plane pencil*  $(A, a)$  is projected out of  $M$  on  $a'$  in the *plane pencil* round  $M^*$ ; this is therefore projective with  $(A', a')$ .

Consequently  $\alpha'$  contains a *conic*  $\sigma^2$  through  $A'$  and  $M^*$  of which all the points  $R'$  are *singular* and each is the *image* of a *complex-cone* that has its vertex in  $\alpha$ .

The conic  $\sigma^2$  is projected out of  $M$  on  $\alpha$  in a conic passing through  $A_0$  (passage of  $k'$ ) and  $A$ . Because  $a'$  cuts the line  $MR$ , there passes through  $a'$  a plane  $\varrho'$  which contains  $MR$ ; accordingly  $R$  is a point of

the conic  $\alpha^2$  and  $\alpha^2$  is the *central projection* of  $\alpha^2$  out of  $M$  as center.

If  $R$  is a point of  $\alpha^2$ , the tangent plane  $\varrho$  through  $a \equiv RA$  to the complex-cone of  $R$  defines a plane  $\varrho'$  through  $a'$ ; the image  $\varrho^2$  of  $\alpha^2$  contains, therefore, the point  $R'$  of  $\alpha^2$ . Consequently  $\alpha^2$  is a curve of  $\mathbf{A}^3$ ; together with  $d$  it forms the intersection with  $\alpha'$ .

The *singular conic*  $\alpha^2$  is the *image* of a *congruence* [4, 4] which has  $\alpha^2$  as *directrix*. For through a point  $X$  there pass the generatrices of the complex-cone of  $X$  which rest on  $\alpha^2$ ; a plane  $\xi$  contains two points of  $\alpha^2$ , hence four rays  $r$ .

6. A ray  $a$  contains three singular points  $S$  of  $\mathbf{Q}$  outside  $A$ . One of the plane pencils of  $S$  passes through  $a$ ; all the rays of this plane pencil cut  $a$  in  $S$  and have the same plane  $\varrho$ . Accordingly the point of intersection  $S'$  of  $MS$  with  $\varrho'$  is *singular* and the image of the plane pencil.

The locus of  $S$  is the intersection of  $a$  with the singular surface  $\Sigma^4$  of  $\mathbf{Q}$ , hence a curve  $\sigma^4$  that has a node in the point where  $\Sigma^4$  is touched by  $a$ . The planes  $\varrho$  envelop the tangent cone  $K_4$  of the 4th class which has  $A$  as vertex; likewise the homologous planes  $\varrho'$  envelop a cone of the 4th class,  $K_4'$ , with vertex  $A'$ . To each generatrix of the cone  $(M, \sigma^4)$  a tangent plane  $\varrho'$  of  $K_4$  is associated and inversely. As  $M$  lies in four planes  $\varrho'$ , the locus of  $S'$  has a quadruple point in  $M$ . A plane through  $M$  contains four more points  $S$ .

There is therefore a *singular twisted curve*  $\sigma^8$  with *quadruple point*  $M$  of which each point represents a *plane pencil* which contains a ray of  $(A, a)$ .

These plane pencils form together a *congruence* [4, 4]\*. The curve  $\sigma^8$  lies on  $\mathbf{A}^3$ , for each of its points is among others the image of a ray of  $(A, a)$ .

7. The *complex-cone* of a point  $T$  cuts  $a$  along a conic  $\tau^2$ . Any plane  $\varrho$  through  $t \equiv AT$  contains two rays  $r_1, r_2$ , hence the homologous plane  $\varrho'$  through  $t'$  two points  $R'$ . To the plane  $Mt'$  there corresponds a plane  $\varrho$  which contains two generatrices of  $(T, \tau^2)$  both of which are represented in  $M$ . A plane through  $M$  contains two more points  $R$ , hence two points  $R'$ .

The *image* of a *complex-cone* is accordingly a *twisted curve*  $\tau^4$  with *node*  $M$ . The curve  $\tau^4$  cuts  $\sigma^8$  and  $\sigma^2$  each in *four* points, for the cone  $(T, \tau^2)$  contains four rays of the congruence [4, 4]\* and four rays which cut  $\alpha^2$ .

If  $T$  is a *point* of  $a$ , the image of its complex-cone consists of the point-range on  $MT$ , the point-range on a straight line of  $\alpha'$  (image of  $TA^*$ ), and a conic  $\varrho_0^2$  (image of  $TA$ ).

A *scroll*  $(\tau)^2$  has also for image a *twisted curve*  $\varrho^4$ , which has a *node* in  $M$ .

If  $T$  is a *singular point* of  $\mathbf{Q}$ , the complex-cone has a double gene-

matrix and consists of two plane pencils. The *image* of a *complex-plane pencil* is a conic  $\varrho^2$  through  $M$  which cuts  $\sigma^2$  and  $\sigma^8$  each twice.

A *complex-conic*  $\gamma^2$  is represented by a plane curve. The axial congruence [2,2] which has  $k$  for axis (§ 4), contains two tangents to  $\gamma^2$ ; hence  $M$  is a node of the image curve. Each point  $R$  of the line of intersection of  $a$  with the plane  $\gamma$  of  $\gamma^2$  corresponds to two rays  $r$ ; accordingly  $MR$  contains two points  $R'$ . The points of intersection of  $\gamma$  and  $a^2$  lie each on two rays  $r$ , which have the same point of  $\sigma^2$  for image.

Consequently the *complex-rays* of a plane  $\gamma$  are represented by the points of a *plane curve*  $\gamma^4$  which has  $M$  and two points of  $\sigma^2$  as *nodes*. In four points it rests on  $\sigma^8$ , for four rays belong to the congruence [4,4]\*.

If  $\gamma$  is a *singular plane* of  $\mathbf{Q}$ , each of the plane pencils has a conic  $\varrho^2$  as image. Two of the four points of intersection of these conics lie on  $\sigma^2$ , one in  $M$ ; the fourth is the image of the common ray of the plane pencils.

8. The rays of  $\mathbf{Q}$  which belong to a linear complex, form a congruence [2, 2]. Its image has two points  $R'$  outside  $M$  in common with a ray  $MR$ ; they are the images of the rays through  $R$ . The rays of the [2, 2] that rest on  $k$ , form a scroll of the fourth order; its intersection with  $a$  consists of the ray  $a$  of the linear complex and a cubic. The generatrices of the cone that projects this curve out of  $M$ , touch the image surface at  $M$ .

Consequently the congruence [2, 2] is represented on a surface  $\mathbf{B}^5$  with *triple point*  $M$ .

This surface has  $a^2$  as *nodal curve*, passes through  $MA$  and contains  $\sigma^8$ .

9. The rays of  $\mathbf{Q}$  which cut two lines  $b$  and  $c$ , form a scroll  $(r)^4$  with double directrices  $b$  and  $c$ . They are projected out of  $A$  by the tangent planes  $\varrho$  of a cone of the 4<sup>th</sup> class. Also the corresponding planes  $\varrho'$  form a system with index 4; hence  $M$  is a quadruple point of the image curve. The passages  $R$  of the rays  $r$  are projected out of  $M$  by a cone of the fourth order with two double generatrices. Accordingly the *image* of  $(r)^4$  is a *twisted curve*  $\varrho^8$  with *quadruple point*  $M$  which cuts each of the curves  $\sigma^2$  and  $\sigma^8$  eight times.

10. A point-range  $(R')$  on the line  $g'$  is the image of a scroll  $(r)$  which has the projection  $g$  of  $g'$  out of  $M$  as directrix. As  $g'$  contains five points of  $\mathbf{B}^5$ , there are five rays  $r$  which rest on  $b$ .

Hence  $g'$  is the *image* of a scroll  $(r)^5$ .

Three rays of  $(A, a)$  and one ray of  $(A^*, a)$  belong to  $(r)^5$ ; they form with  $g$  the intersection with  $a$ .

11. A *field of points*  $[R']$  is the image of a congruence [4, 4].

For the image of a complex-conic (complex-cone) contains four points  $R$ . The congruence has double rays in the lines of  $(A, a)$ , contains the plane pencils  $(A, a^*)$  and  $(A^*, a)$  and also the scroll  $(s)^5$  of the singular rays. It has two singular points of the second order on  $a^2$  and eight singular points of the first order, which are at the same time singular points of  $Q$ .

12. The plane pencils of  $Q$  are represented in a double infinite system of conics  $\varrho^2$  (§ 7). Through an arbitrary point  $R'$  there pass *four* conics, for the ray  $r$  that has  $R'$  as image, belongs to four plane pencils. If  $R'$  lies on the cone  $(M, a^2)$ , each of these conics consists of the line  $MR'$  and a second straight line.

Through each point of  $\sigma^2$  and  $\sigma^3$  there pass  $\infty$  curves  $\varrho^2$ ; these points are, therefore, *singular* for the congruence  $[\varrho^2]$ ; this congruence has  $M$  as *cardinal point*. Each plane through  $M$  contains *eight* conics; for its line of intersection with  $a$  carries *four* singular planes of  $Q$ . Any line  $C$  is therefore a chord of eight  $\varrho^2$ , and the  $\varrho^2$  resting on  $l$  form a surface of the order 20.

**Mathematics.** — "A Representation of the Rays of Space on a System of Conics". By Prof. JAN DE VRIES.

(Communicated at the meeting of January 31, 1925).

1. Through axial projection a twisted cubic  $\varrho^3$  may be represented on a conic  $\varrho^2$ . The pencil of planes that has a straight line  $l$  as axis, defines on  $\varrho^3$  the triples  $A_1, A_2, A_3$  of an involution  $I^3$ . If  $B_k$  is the image of  $A_k$ , the triples  $B_1, B_2, B_3$  on  $\varrho^2$  also form an  $I^3$ . The tangents  $b_1, b_2, b_3$  to  $\varrho^2$  at  $B_1, B_2, B_3$  define a triangle with angular points  $C_1, C_2, C_3$ ; the locus of the points  $C_k$  is a conic  $\lambda^2$  (*involutorial conic* of the  $I^3$ ). We consider  $\lambda^2$  as the *image* of the line  $l$ .

Let  $\lambda^2$  be a conic circumscribed about a tangent-triangle  $C_1C_2C_3$  of  $\varrho^2$ . To the points of  $C_k$  there correspond three points  $A_k$  of  $\varrho^3$ , which define a plane  $\alpha$ . Through a point  $P$  of  $\lambda^2$  there pass two tangents to  $\varrho^2$ ; the points of  $\lambda^2$  that are represented in the points of contact, define a chord  $p$  of  $\varrho^3$ . Analogously a chord  $q$  of  $\varrho^3$  corresponds to a point  $Q$  of  $\lambda^2$ . The line  $l$  of  $\alpha$  resting on  $p$  and  $q$ , is the axis of a pencil of planes, and defines therefore an  $I^3$  on  $\varrho^3$ . The involutorial conic corresponding to this  $I^3$ , passes through the points  $C_1, C_2, C_3, P$  and  $Q$ ; hence  $\lambda^2$  is the *image* of  $l$ .

Through *four* points there pass *two* conics  $\lambda^2$ . For these points define four chords of  $\varrho^3$  and these have two transversals  $l$ . To the involutions defined by them there correspond conics  $\lambda^2$  which pass through the given points.

2. If  $l$  cuts the curve  $\varrho^3$ ,  $I^3$  consists of the pairs of an  $I^2$ , which are completed to triples by a fixed point. The conic  $\lambda^2$  is in this case the combination of a tangent  $r$  to  $\varrho^2$  and the involutorial line  $\lambda$  of an  $I^2$ .

The  $I^2$  on  $\varrho^3$  corresponds to an infinite number of secants  $l$ ; these form the second scroll on the hyperboloid of the bisecants defined by  $I^2$ . The corresponding pairs of lines  $\lambda^2$  have the involutorial straight line  $\lambda$  in common. The *complex of the secants* is accordingly represented on the  $\infty^3$  pairs of lines each of which consists of a tangent  $r$  and a line  $\lambda$ .

The image of a bisecant of  $\varrho^3$  is a pair of lines formed by two tangents  $r_1, r_2$  of  $\varrho^2$ . The congruence [1, 3] of the *bisecants* is, therefore, represented on the  $\infty^2$  pairs  $r_1, r_2$ .

3. If  $l$  describes a *plane pencil* ( $l$ ), the corresponding involutions have in common the group in the plane of the pencil and the pair on the

bisecant through the vertex of the pencil. The *image-conics*  $\lambda^2$  form a *pencil*; three of the base points lie in the angular points of a triangle circumscribed about  $\lambda^2$ . The *three pairs of lines* are the images of the *three secants* belonging to  $(l)$ .

A *field of rays*  $[l]$  has for image a *net*  $[\lambda^2]$  with *three base points* (angular points of a triangle circumscribed about  $\varrho^2$ ).

4. If a *net* of conics has *three arbitrary base points*, the curves  $\lambda^2$  of the involution contained in it form the image of a *quadratic scroll*  $(l)^2$ . For the corresponding lines  $l$  must rest on three fixed chords of  $\varrho^3$ . The six secants belonging to  $(l)^2$  have pairs of lines as images.

An *arbitrary scroll*  $(l)^2$  is represented in a system  $(\lambda^2)_2$  with *index two*. For on each chord of  $\varrho^3$  there rest two lines  $l$ ; hence two curves  $\lambda^2$  pass through the pole of the image chord. There are six pairs of lines corresponding to the secants which cut  $\varrho^3$  in its points of intersection with  $(l)^2$ .

A *sheaf*  $[l]^*$  is represented in a *net* of conics  $\lambda^2$  which pass through *one* fixed point, the pole of the chord corresponding to the bisecant through the vertex of the sheaf.

For through any two points there passes a  $\lambda^2$ ; it is the image of the ray of the sheaf which cuts the two corresponding chords of  $\varrho^3$ .

5. On an arbitrary line  $l$  there rest four tangents to  $\varrho^3$ ; two of the corresponding triangles circumscribed about  $\varrho^2$  coincide in a point of intersection of  $\lambda^2$  and  $\varrho^2$ .

If  $l$  lies in a *plane of osculation*  $\omega$  of  $\varrho^3$ , two nodes of the  $I^3$  defined by  $l$  coincide in the point of contact of  $\omega$ ; the conics  $\lambda^2$  and  $\varrho^2$  touch each other.

If  $l$  is the intersection of two planes of osculation, it is represented by a  $\lambda^2$  which touches  $\varrho^2$  twice.

The *congruence* [3,1] of the *axes of osculation* is accordingly represented in the system of the conics of the involution which touch  $\varrho^2$  twice. Such a  $\lambda^2$  is defined by its points of contact.

If  $l$  is an *osculating ray*, hence a secant lying in the plane of osculation of its point of intersection, one of the nodes of the  $I^2$  lies in that point; the line  $\lambda$  of the involution passes through the point of contact of  $r$ .

The *congruence* [3,3] of the *osculating rays* is represented on the  $\infty^2$  pairs of lines formed by a tangent of  $\varrho^2$  and a straight line through the point of contact.

6. A *pencil*  $(\lambda^2)$  of which three base points define a triangle circumscribed about  $\varrho^2$ , contains three curves which touch  $\varrho^2$ . For the corresponding *plane pencil*  $(l)$  contains three rays that are intersections with planes of osculation through the vertex of the plane pencil. Besides  $(\lambda^2)$

contains three pairs of lines touching  $\varrho^2$  which belong to the secants of  $(l)$ .

If the vertex of the pencil is the null-point of its plane, the three secants belonging to  $(l)$  are osculating rays and the base points of the pencil ( $\lambda^2$ ) are the angular points of a triangle circumscribed about  $\varrho^2$  besides the point of intersection of the lines which join the angular points to the points of contact of the opposite sides.

7. The image of a congruence [1,1] is an  $\infty^2$  system of conics  $\lambda^2$ , two of which pass through any two points; they are the images of the rays resting on two chords of the  $\varrho^3$ .

A net [ $\lambda^2$ ] with one or three base points contains one  $\lambda^2$  of the system; it is the image of the ray that passes through a given point or lies in a given plane (§ 4, § 3).

The plane pencils of the congruence are represented by pencils ( $\lambda^2$ ) (§ 3). Their base points lie on the images of the two directrices, three on one of those conics, the fourth on the other conic.

To the [1, 1] there belongs a scroll  $(l)^6$  formed by secants of the  $\varrho^3$ . The lines of the involution  $\lambda$  envelop a curve of the fourth class, for the rays which rest on a chord of  $\varrho^3$ , form an  $(l)^2$  and this cuts  $\varrho^3$  in four more points.

A congruence [1,1] that has two chords of the  $\varrho^3$  as directrices, is represented in an  $\infty^2$  system with two base points; two curves pass through any two points. The quadratic scroll of the secants belonging to the congruence, is represented in the pairs of lines consisting of the join of the base points and a tangent to  $\varrho^2$ .

8. On four chords of  $\varrho^3$  there rest two transversals  $l$ . If the chords  $k_1, k_2, k_3$  are given, we can choose a fourth chord  $k$  so that the two transversals coincide; in this case  $k$  must touch the hyperboloid with directrices  $k_1, k_2, k_3$ . Through a point  $R$  of  $\varrho^3$  there pass four chords  $k$ ; they are the common generatrices of the cone which projects  $\varrho^3$  out of  $R$  and the cone of the tangents through  $R$  to the hyperboloid. Accordingly an arbitrary chord of  $\varrho^3$  rests on the eight chords; the locus of  $k$  is, therefore, a scroll  $(k)^8$  with quadruple curve  $\varrho^3$ .

In order to find the order of the image curve, we consider a straight line of the image plane. The polar lines of its points are the images of a scroll formed by chords of  $\varrho^3$ . This scroll has in common with  $(k)^8$  the curve  $\varrho^3$ , which is to be counted four times; the rest of the intersection must consist of four chords. Hence the scroll  $(k)^8$  is represented on a curve of the fourth order.

It is the curve which is enveloped by the conics of the involution with three base points. For these form (§ 1) a system with index two.

**Mathematics.** — "A Representation of the Rays of Space on the Pairs of Points of a Plane". By Prof. JAN DE VRIES.

(Communicated at the meeting of February 28, 1925).

§ 1. Let  $l$  be an arbitrary straight line which cuts the planes  $a'$  and  $a''$  in the points  $L'$  and  $L''$ .  $L'$  and  $L''$  are projected on the plane  $a$  out of the fixed points  $A'$  and  $A''$ ; the projections  $L_1$  and  $L_2$  form a pair of points which we consider as the image of the ray  $l$ . Apparently two arbitrary points  $L_1$  and  $L_2$  of  $a$  generally define one ray.

Let  $G$  be a point of the intersection  $g$  of the planes  $a'$  and  $a''$ ; all the rays of the sheaf round  $G$  are represented in the pair of points  $G_1, G_2$ , which we call a *cardinal pair*. The cardinal pairs form two projective point-ranges on the lines  $g_1$  and  $g_2$  (the projections of  $g$  out of  $A'$  and  $A''$ ); these meet in the point of intersection  $G_{12}$  of  $g$  and  $a$ . Accordingly the point-ranges  $(G_1)$  and  $(G_2)$  lie *perspectively*; the center of perspectivity  $A_{12}$  is the point of intersection of  $a$  and the line  $a$  which joins the centers  $A'$  and  $A''$ .

Any two points of  $g$  may be considered as intersections with  $a'$  and  $a''$ . Hence any pair consisting of an arbitrary point  $G_1$  and an arbitrary point  $G_2$  may be considered as the image of the *cardinal ray*  $g$ .

If  $l$  lies in  $a'$ ,  $L'$  is an arbitrary point of  $l \equiv l'$ ; if  $G_2$  is the projection of the point  $gl$ , the image of  $l$  consists of  $G_2$  and an arbitrary point  $L_1$  of the line  $l_1$  (the projection of  $l$  out of  $A'$  as center).

The rays in  $a'$  and  $a''$  are, therefore, *singular rays*.

§ 2. The image of a straight line  $d$  cutting  $a$  consists of two points  $D_1, D_2$ , that are collinear with  $A_{12}$ . The pairs of points on a line  $d_{12}$  through  $A_{12}$  are the images of the rays in a plane through  $a$ .

The pairs of points  $L_1, L_2$  on an arbitrary line are the images of the rays of a bilinear congruence of which the directrices lie in  $a'$  and  $a''$ .

The image of a *field of rays* consists of the  $\infty^2$  pairs of points  $L_1, L_2$ , of which  $L_1$  lies on a straight line  $f_1$ ,  $L_2$  on a straight line  $f_2$ . One of these pairs is formed by the images  $G_1, G_2$  of the plane pencil of the rays resting on  $g$ .

The point of intersection  $D_{12}$  of  $f_1$  and  $f_2$  is the image of a ray  $d$  which cuts  $a$ . The *congruence* of the rays for which the images  $L_1$  and  $L_2$  coincide, has accordingly one ray in any plane.

If  $D_{12}$  describes a straight line  $d_{12}$ , the points  $D'$  and  $D''$  describe two projective point-ranges in  $a'$  and  $a''$  and  $d$  envelops a conic which

touches  $a$ . Hence through a given point there pass two rays  $d$  of the congruence in question; this has accordingly the symbol [2, 1]. In the plane  $(G_{12}, a)$  the conic degenerates, for  $G_{12}$  is the image of a pencil in that plane.

Consequently the rays with coinciding image points are the tangents of a quadratic cone with vertex  $G_{12}$  which rest on the fixed tangent  $a$ <sup>1)</sup>.

§ 3. *Image of a plane pencil.* The image of a plane pencil is formed by two projective point-ranges on two straight lines  $f_1, f_2$ . One pair consists of the image  $G_1, G_2$  of the ray resting on  $g$ , and another pair,  $D_1, D_2$ , is the image of the ray that cuts  $a$ .

If we choose the line  $f_1$  at random and if  $G_1$  is its intersection with  $g_1, G_2$  the point which forms a cardinal pair with  $G_1, f_2$  must pass through  $G_2$ . If we associate two arbitrary points  $P_2, Q_2$  of  $f_2$  to two arbitrary points  $P_1, Q_1$  of  $f_1$ , and if  $G_2$  corresponds to  $G_1$ , the point-ranges on  $f_1$  and  $f_2$ , which in this way have become projective, are the image of a plane pencil.

The projective point-ranges on  $f_1$  and  $f_2$  define a conic  $\delta^2$  as the envelope of the lines  $l_{12} \equiv L_1 L_2$ . One of the tangents through  $A_{12}$  contains the cardinal pair  $G_1, G_2$ , the other the pair  $D_1, D_2$ . If we consider  $\delta^2$  as the image of the plane pencil, the  $\infty^5$  plane pencils of space are represented on the  $\infty^5$  conics of a plane.

But in this way any conic is the image of two plane pencils; for each of the two tangents through  $A_{12}$  may be considered as  $g_{12} \equiv G_1, G_2$ , the other containing the pair  $D_1, D_2$ . The tangents through  $G_1$  and  $G_2$  define the carriers  $f_1, f_2$  of the projective point-ranges.

By means of the conics  $\delta^2$  we find accordingly an involution in the plane pencils of space.

If the vertex  $T$  of a plane pencil lies in  $a'$ ,  $\delta^2$  degenerates. For in this case the image consists of the pairs formed by  $T_1$  and the points  $L_2$  of a straight line  $f_2$  and of the pairs formed by the point  $G_2$  on  $f_2$  and the points  $L_1$  of  $f_1$ .

If the whole plane pencil lies in  $a'$ , each ray has  $\infty^1$  images consisting of a point  $G_2$  and a point of a definite ray of the plane pencil round  $T_1$ .

If the plane of the pencil passes through  $G_{12}$ , its image consists of two perspective point-ranges and  $\delta^2$  degenerates into two plane pencils. If the plane passes through  $a$ , the image consists of two collocal projective point-ranges.

§ 4. *Image of a quadratic scroll.* The image is formed by two projective point-ranges on two conics  $a_1^2$  en  $a_2^2$ . The points of intersection of  $a_1^2$  and  $g_1$  form cardinal pairs with the points where  $a_2^2$  is cut by  $g_2$ ;

<sup>1)</sup> A congruence [1,2] consists of the transversals of a conic and a fixed straight line cutting it. A [2,1] corresponds to it dually.

these pairs are the images of the rays that rest on  $g$ . The two rays resting on  $a$  have images  $L_1, L_2$ , for which  $l_{12}$  passes through  $A_{12}$ .

Let  $u_1^2$  be an arbitrary conic,  $G_1$  and  $G_1^*$  its points of intersection with  $g_1$ . If we pass a conic  $u_2^2$  through  $G_2$  and  $G_2^*$  and establish a projective correspondence between the point-ranges on  $u_1^2$  and  $u_2^2$  so that  $G_1$  and  $G_1^*$  are associated to  $G_2$  and  $G_2^*$ , we have obtained the image of a quadratic scroll. If the scroll has a *directrix*  $f'$  in  $u'$  and a *directrix*  $f''$  in  $u''$ , its image is formed by two projective point-ranges on the lines  $f_1$  and  $f_2$ . In this case the points  $f_1 g_1$  and  $f_2 g_2$  do not form a cardinal pair. To the image there belong also the pairs of points which represent the rays of the scroll in  $u'$  and  $u''$ .

§ 5. *Image of a sheaf.* The rays through the point  $S$  make the fields of points  $[L']$  and  $[L'']$  perspective. Accordingly the image of the sheaf is formed by the pairs  $L_1, L_2$  of two projective fields.

The plane pencil of the rays resting on  $g$ , has its image in the *cardinal pairs*. To the sheaf there belong two rays of the congruence  $[2, 1]$ , the rays of which are represented by points  $D_{12}$ . These two points and the point  $G_{12}$  are the *coincidences* of the two fields.

If the projective correspondence between the points of the fields  $[L_1]$  and  $[L_2]$  is such that the cardinal pairs consist of homologous points, we have the image of a sheaf. In order to see this we investigate what this image,  $\mathbf{B}$ , has in common with the image  $\mathbf{V}$  of a field of rays and with the image  $\mathbf{S}$  of an arbitrary sheaf.

The image  $\mathbf{V}$  consists of the  $\infty^2$  pairs  $L_1, L_2$  on two lines  $f_1, f_2$ . The straight line  $f_2^*$  which is associated to  $f_1$  in  $\mathbf{B}$  cuts  $f_2$  in the point  $G_2$  which is associated to the point  $G_1$  on  $f_1$ . Hence  $\mathbf{V}$  and  $\mathbf{B}$  have only this pair  $(G_1, G_2)$  in common. But a cardinal pair is the image of a sheaf (round  $G$ ); accordingly the field of rays generally does not contain any ray of the congruence that has  $\mathbf{B}$  as image.

Let  $L_1, L_2$  be a pair of  $\mathbf{B}$ ,  $L_1^*$  the point which through  $\mathbf{S}$  is associated to  $L_2$ . In this case the points  $L_1$  and  $L_1^*$  are homologous in a projectivity that has all the points of  $g_1$  as double points and is, therefore, a *homology*.

The center of the homology is a point  $L_1$  to which  $\mathbf{B}$  and  $\mathbf{S}$  associate the same point  $L_2$ . But then  $\mathbf{B}$  must be the image of a congruence  $[0, 1]$ , hence of a sheaf.

§ 6. Let us suppose that a *homology* in  $a$  contains the cardinal points; these are the images of the rays of the congruence that is represented by the homology.

A ray of this congruence which cuts  $a$ , has for image a pair  $D_1, D_2$ . The line  $d_{12}$  through  $D_1$  and  $D_2$  contains also a cardinal pair and is, therefore, a double ray of the homology; accordingly this has  $A_{12}$  for center and its axis passes through  $G_{12}$ . The point-ranges on homologous

lines are projective, hence images of a plane pencil that has  $a$  as a ray. Consequently the homology in question is the *image* of a *parabolic congruence* [1,1] that has  $a$  as *directrix*.

§ 7. *Image of a bilinear congruence.* The rays of a congruence [1,1] define a *quadratic correspondence* in  $a$ . For the line  $f'$  of  $a'$ , which is the projection of a line  $f_1$  in  $a$ , defines, together with the directrices  $r$  and  $s$  of the congruence, a quadratic scroll, hence a conic  $q''$  in  $a''$ , consequently also a conic  $q_2$  in  $a$ . The ray  $t'$  of the [1,1] that lies in  $a'$ , defines a point  $G^*$  on  $g$ . Hence  $q_2$  passes through  $G_2^*$  and through the images  $R_2$  and  $S_2$  of  $r$  and  $s$ . These three points are the *cardinal points* of the latter system. The *cardinal points* of the former system are  $R_1, S_1$  and the image  $G_1^*$  of the ray in  $a''$ .

The plane pencil of the congruence that has  $R'$  as vertex, has for image the point-range on  $S_2G_2^*$ , apart from the image of  $t'$ . Together with the point-range on  $R_1S_1$  the cardinal point  $G_2^*$  forms the image of the ray  $t'$ .

The plane pencils of the [1,1] that have their vertices on  $s$ , are represented in the point-ranges on lines  $f_1$  and  $f_2$  of which  $f_1$  passes through  $R_1$  and  $f_2$  through  $R_2$ ; the plane pencil ( $f_1$ ) is projective with the plane pencil ( $f_2$ ). Analogously  $S_1$  and  $S_2$  are the centers of two projective plane pencils, and any two homologous rays contain the image of a plane pencil that has its vertex on the directrix  $r$ .

A *parabolic* [1,1] consists of  $\infty^1$  plane pencils which have a ray  $r$  in common while the vertices form a point-range on  $r$  which is projective with the pencil of their planes. The quadratic scroll which has a line of  $a'$  as directrix, contains a ray of the plane pencil of the [1,1] that has  $R''$  as vertex. The plane of this pencil touches the carrier of the scroll at  $R''$ ; accordingly the conics  $q''$  have a fixed tangent at  $R''$ . But then the conics  $q_2$  have also the same tangent at  $R_2$ . Consequently the *quadratic correspondence* has *two coinciding cardinal points* in  $R_2$ ; this is also the case in  $R_1$ . This result could be foreseen because in this case the directrix  $s$  coincides with  $r$ .

§ 8. We arrive at an *involution* in the *rays of space* by associating to a ray  $l$  with image  $L_1, L_2$  the ray  $m$  of which the image consists of the points  $M_1 \equiv L_2$  and  $M_2 \equiv L_1$ .

If  $l$  describes a plane pencil,  $L'$  and  $L''$  describe projective point-ranges; hence  $L_1$  and  $L_2$  describe projective point-ranges on two lines  $l_1$  and  $l_2$ . The points  $G_1 \equiv g_1 l_1$  and  $G_2 \equiv g_2 l_2$  form a cardinal pair. But this is not the case with the points  $H_1 \equiv G_2$  and  $H_2 \equiv G_1$ ; hence the point-ranges  $(M_1)$  on  $m_1 \equiv l_2$  and  $(M_2)$  on  $m_2 \equiv l_1$  form the representation of a quadratic scroll. Accordingly our *involution* transforms a plane pencil into a *quadratic scroll*.

The double rays of this involution form the congruence [2,1] found in § 2.

The rays in a plane through  $a$  are arranged in involutorial pairs.

To the ray  $g$  there corresponds the field of rays in the plane defined by  $h_1 \equiv g_2$  and  $h_2 \equiv g_1$ .

§ 9. As we pointed out, the conics  $\delta^2$  give rise to an *involution* in the *plane pencils of space*.

In this way each of the two systems of plane pencils of a congruence [1,1] is transformed in itself. Let us consider e.g. the pencils in the planes through the directrix  $r$ , which, therefore, have their vertices on the directrix  $s$ . Let  $\delta^2$  be the image of such a plane pencil; one of its tangents through  $A_{12}$ ,  $G_{12}$ , contains a cardinal pair  $G_1, G_2$ , the other,  $d_{12}$ , contains the image  $(D_1, D_2)$  of the ray of the pencil that rests on  $a$ . The straight lines  $f_1 \equiv R_1 G_1$  and  $f_2 \equiv R_2 G_2$  carry the image points  $L_1, L_2$  of the other rays of the pencil.

If we also draw the tangents  $f_1^*$  and  $f_2^*$  through  $R_1$  and  $R_2$ , these contain the images of the rays of another plane pencil belonging to the system; now  $d_{12} \equiv g_{12}^*$  contains the cardinal pair  $G_1^*, G_2^*$ ,  $g_{12} \equiv d_{12}^*$  the pair  $(D_1^*, D_2^*)$ .

Any tangent  $l_{12}$  to  $\delta^2$  contains the image  $(L_1, L_2)$  of a ray of the former plane pencil and the image  $(L_1^*, L_2^*)$  of a ray belonging to the latter. The line  $l_{12}$  contains the images of the rays of a congruence [1,1] that has as directrices a straight line of  $a'$  and one of  $a''$ . This congruence has two lines in common with the given [1,1]; each of them belongs to one of the plane pencils in question.

An arbitrary line of  $a$  is, therefore, touched by one  $\delta^2$ ; accordingly the conics of our system form a *scroll*. The two conics meeting in  $A_{12}$ , are the images of the plane pencils lying in the double planes of the involution round  $r$ .

The *pairs of points* of the scroll are  $(S_1, G_2^*), (S_2^*, G_1)$  and the pair to which  $G_{12}$  belongs.

If the congruence [1,1] is *parabolic* with the directrix  $r$ , the conics of the system have the line  $R_1 R_2$  as common tangent.

§ 10. Let us now consider the system  $\Sigma$  of the *plane pencils* with *common ray*  $r$  that have their *vertex* in the point  $S$  (and which belong, therefore, to the sheaf round  $S$ ).

All the conics  $\delta^2$  touch the straight line  $r_{12} \equiv R_1 R_2$  and the intersection  $d_{12}$  of their planes and the plane  $(Sa)$ ; for each plane pencil has one ray in the latter plane and the images of these rays form two projective point-ranges on  $d_{12}$ .

Now to any plane pencil there corresponds the plane pencil of the rays that have their images on the tangents  $f_1^*, f_2^*$  through the points  $G_1^*, G_2^*$  on  $d_{12}^*$ . The new pencils form a congruence  $\Sigma^*$ ; their planes pass through the point  $G^*$ . Evidently the plane pencils  $(f_1^*)$  and  $(f_2^*)$  are projective; hence the lines  $f'$  and  $f''$  (in  $a'$  and  $a''$ ) describe two

projective plane pencils round  $G^*$  and the *planes* of the pencils of  $\Sigma^*$  envelop a *quadratic cone*. Consequently an arbitrary point lies on *two* rays of the pencils and an arbitrary plane contains *one* ray.

The system  $\Sigma$  is transformed by the involution into a *congruence* [2,1].

§ II. Let  $\Sigma$  be the system of the *pencils* in a *plane*  $\varrho$  that have one *ray*  $r$  in common. If the field of rays in  $\varrho$  is represented by the pairs of points on  $f_1$  and  $f_2$ , the plane pencils of  $\Sigma$  have as images the conics which touch  $f_1, f_2, r_{12}$ , and  $g_{12}$ , which form accordingly a *scroll*.

Any line  $d_{12}$  defines one  $\delta^2$ ; the tangents  $f_1^*$  and  $f_2^*$  through the points  $G_1^*$  and  $G_2^*$  on  $d_{12}$  contain the images of the rays of the associated plane pencil. Any plane contains one ray of the system  $\Sigma^*$ .

Let  $L_1$  be a point of  $u$ ,  $G_1$  a point of  $g_1$ ,  $\delta^2$  the conic which touches  $L_1 G_1$ . The tangent  $d_{12}$  cuts  $g_1$  in a point  $G_1^*$ , which we associate to  $G_1$ . If we choose  $G_1^*$  arbitrarily on  $g_1$ ,  $A_{12} G_1^*$  defines a  $\delta^2$  of which two tangents meet in  $L_1$ . Hence  $g_1$  contains *three* points  $G_1^*$  for which  $A_{12} G_1^*$  and  $L_1 G_1^*$  touch the same  $\delta^2$ . Each of the three lines  $f_1^* \equiv L_1 G_1^*$  corresponds to a plane pencil of  $\Sigma^*$ . Accordingly this system is a *congruence* [3,1].

It consists of the *pencils* in the *planes of osculation* of a *twisted cubic* of which the *vertices* lie on the intersection of two planes of osculation <sup>1)</sup>.

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<sup>1)</sup> This congruence corresponds dually to the [1,3] which has a twisted cubic and one of its bisecants as directrices. The other [1,3] which consists of the bisecants of a curve  $\mathcal{C}^3$ , does not contain any plane pencils.

**Mathematics.** — “*Sur les correspondances planes symétriques [2,2] de la première classe, résultantes de couples de points conjugués par rapport à une conique*”. (Lettre de Mr. E. VENERONI à Mr. JAN DE VRIES).

(Présenté par M. le Prof. JAN DE VRIES à la séance du 30<sup>me</sup> mai 1925).

Vous avez étudié, dans la Note „*Involutorial correspondences [2,2] of the first Class*”<sup>1)</sup> une remarquable correspondance plane symétrique [2,2] de la première classe,  $\Gamma$ ,<sup>2)</sup> résultante des couples de points conjugués par rapport à une conique donnée,  $a^2$ , situés sur les coniques d'un faisceau ( $b^2$ ).

Permettez que je Vous démontre comment on peut aussi l'obtenir, en particulierisant quelques correspondances que j'avais déjà rencontrées<sup>3)</sup> à savoir:

1. Les  $\Gamma$  possédant quatre points singuliers et quatre droites singulières, indépendantes, de la première espèce<sup>4)</sup>.

2. Les  $\Gamma$  qui sont douées de dix droites singulières de la première espèce, et qui, par conséquent résultent de couples de points conjugués par rapport à une conique<sup>5)</sup>.

J'aurai, ainsi, l'occasion d'indiquer une construction de toutes les  $\Gamma$  résultantes de couples conjugués par rapport à une conique, aussi générale mais bien plus simple que celle que j'ai donné dans les notes mentionnées, qui est fondée sur les propriétés de la congruence [7,2] de droites et de sa surface focale.

Je veux bien ajouter, à mon tour, que la  $\Gamma$  engendrée par les couples de points conjugués par rapport à une cubique plane, signalée au § 3 de ma note  $b$ , avait été déjà étudiée par Vous, dans votre Note „*On pairs of points which are associated with respect to a plane cubic*”<sup>6)</sup>.

§ 1. On peut construire toute  $\Gamma$  possédant quatre droites singulières  $s_i$  et quatre points singuliers,  $B_i$ , indépendants, en rapportant projecti-

<sup>1)</sup> These Proceedings, Vol. 24, 1921, p. 12—16.

<sup>2)</sup> On désignera avec  $\Gamma$  toute correspondance plane symétrique [2,2] de la première classe.

<sup>3)</sup> Dans mes notes:

a. *Sulle corrispondenze piane simmetriche [2,2] della classe uno*;

b. *Principali tipi di corrispondenze piane simmetriche [2,2] della classe uno* (Rendiconti del R. Istituto Lombardo di Scienze e Lettere, Milano, Vol. LI, 1918 pp. 374—387 et pp. 753—777.

<sup>4)</sup> Voir note  $b$ , § 2.

<sup>5)</sup> Voir note  $b$ , § 3, 4, 5.

<sup>6)</sup> These Proceedings, Vol. 12, 1910, p. 711—715.

vement le faisceau de coniques ( $b^2$ ) ayant pour base les points  $B_i$  au faisceau tangentiel de coniques ( $\beta^2$ ) ayant pour base les droites  $s_i$ , et en coupant chaque conique  $b^2$  par les tangentes de la conique correspondante  $\beta^2$ ).

Parmi ces  $\Gamma$  se trouve la Vôtre, car les couples de points correspondants dans Votre  $\Gamma$ , situés sur chaque conique  $b^2$  sont réunis par des droites qui enveloppent une conique  $\beta^2$ ; et, comme la conique  $b^2$  varie dans le faisceau, la conique correspondante  $\beta^2$  varie dans un faisceau tangentiel, ayant pour base les quatre droites singulières que Vous avez indiquées par  $s_k$ .

Il n'est pas inutile de démontrer, réciproquement, quelle doit être la position relative du quadrangle ( $B$ ) et du quadrilatère ( $s$ ) et comment on peut établir la projectivité entre ( $b^2$ ), ( $\beta^2$ ), pour obtenir Votre correspondance.

Il faut, d'abord, choisir ( $s$ ), ( $B$ ) de manière que deux côtés opposés quelconques de ( $B$ ) soient tangentes à une même conique de ( $\beta^2$ ), et déterminer, ensuite, la projectivité entre ( $b^2$ ) et ( $\beta^2$ ), en faisant correspondre à chacune des trois coniques de ( $b^2$ ), qui se réduisent à deux côtés opposés de ( $B$ ), la conique de ( $\beta^2$ ) qui est tangente à ces deux côtés.

On peut obtenir le quadrangle ( $B$ ) et le quadrilatère ( $s$ ) de la manière suivante :

Ayant choisi, arbitrairement, le quadrangle ( $B$ ), considérons une conique  $\beta_1$ , tangente à deux côtés opposés de ( $B$ ),  $B_1B_2$ ,  $B_3B_4$ , et fixons deux autres tangentes quelconques de  $\beta_1$ ,  $s_1$ ,  $s_2$ . Les  $s_1$ ,  $s_2$  et chacun des deux couples de droites  $B_1B_3$ ,  $B_2B_4$ ;  $B_1B_4$ ,  $B_2B_3$  déterminent deux faisceaux tangentiels de coniques; les couples de tangentes, qui, en dehors des  $s_1$ ,  $s_2$ , sont communs à  $\beta_1$  et aux coniques de chaque faisceau, sont conjugués en deux involutions entre les tangentes de  $\beta_1$ ; les deux droites  $s_3$ ,  $s_4$  du couple commun aux deux involutions et les  $s_1$ ,  $s_2$ , sont tangentes à une même conique  $\beta_2$  avec les  $B_1B_3$ ,  $B_2B_4$ , et à une même conique  $\beta_3$  avec les  $B_1B_4$ ,  $B_2B_3$ ; c'est à dire qu'au faisceau tangentiel ( $\beta^2$ ) de coniques, ayant pour base les quatre droites  $s_i$ , appartiennent les trois coniques  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ , tangentes respectivement, aux trois couples de côtés opposés du quadrangle ( $B$ ).

§ 2. Cela posé, on rapporte projectivement le faisceau ( $b^2$ ) au faisceau tangentiel ( $\beta^2$ ), en faisant correspondre aux coniques dégénérées  $B_1B_2$ ,  $B_3B_4$ ;  $B_1B_3$ ,  $B_2B_4$ ;  $B_1B_4$ ,  $B_2B_3$  respectivement les coniques  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ .

En coupant chaque conique de ( $b^2$ ) avec les tangentes de la conique homologue de ( $\beta^2$ ), on obtient les couples d'une  $\Gamma$ , qui est la Vôtre.

Il suffira, en effet, de remarquer qu'on peut obtenir la courbe double de la  $\Gamma$  comme lieu des points de contact de chaque conique de ( $b^2$ ) avec les tangentes de la conique homologue de ( $\beta^2$ ): ce lieu sera, donc, lorsque ( $b^2$ ), ( $\beta^2$ ) sont arbitrairement choisis, une courbe du 8<sup>me</sup> ordre; mais, dans le cas que nous examinons, les six droites  $B_i B_k$  se détachent de la courbe, et le lieu résiduel est une conique  $a^2$ ; c'est donc la conique de BERTINI

par rapport à chaque  $C_M^4$  7); et, puisque les points où les tangentes en  $M$  à  $C_M^4$  rencontrent de nouveau la  $C_M^4$ , sont les points homologues à  $M$  dans  $\Gamma$ , et se trouvent sur la droite polaire de  $M$  par rapport à  $a^2$ , tous les couples de  $\Gamma$  seront conjugués par rapport à la conique  $a^2$ .

§ 3. On en conclut aussi que Votre  $\Gamma$  est caractérisée, entre celles qui possèdent quatre points singuliers  $B_i$  et quatre droites singulières  $s_k$ , indépendants, par la propriété d'avoir de plus, comme droites singulières, les six côtés du quadrangle ( $B$ ).

En effet, lorsqu'on engendre la  $\Gamma$ , comme au § 2, au moyen du faisceau  $(b^2)$  et du faisceau tangentiel  $(\beta^2)$ , le lieu des points qui forment avec  $B_1$  des couples de  $\Gamma$ , est une courbe du quatrième ordre, avec un point triple en  $B_1$ , que l'on peut obtenir en coupant chaque conique  $b^2$  par les tangentes, issues de  $B_1$ , à la conique correspondante de  $(\beta^2)$ ; mais, si les droites  $B_i B_k$  sont singulières, les trois droites  $B_1 B_2$ ,  $B_1 B_3$ ,  $B_1 B_4$  se détachent de la courbe; il faut donc qu'à la conique de  $(b^2)$ , composée des deux droites  $B_1 B_2$ ,  $B_3 B_4$  soit homologue une conique de  $(\beta^2)$  tangente à la droite  $B_1 B_2$ , et, de même, à la  $B_3 B_4$ . On en conclut que la projectivité entre  $(b^2)$  et  $(\beta^2)$  fait correspondre à chacune des trois coniques dégénérées de  $(b^2)$ , qui se réduisent à deux côtés opposés de ( $B$ ), une conique de  $(\beta^2)$ , qui est tangente à ces deux côtés.

La  $\Gamma$ , donc, est bien la Vôtre.

§ 4. Nous avons, tous les deux, remarqué, qu'une  $\Gamma$ , établie entre les points d'un plan, engendre aussi une  $[2,2]$  symétrique entre les droites du plan,  $\Gamma^*$ , qui est, pareillement, de la première classe; les  $\Gamma, \Gamma^*$  se déterminent réciproquement.

Or, des §§ 3, 5 de ma Note  $b$  on déduit que, étant données les  $\Gamma, \Gamma^*$ , associées entre elles, lorsqu'il y a dix droites (ou dix points) singuliers de la première espèce, la  $\Gamma$  (ou la  $\Gamma^*$ ) résulte de couples de points (ou de droites) conjugués par rapport à une conique; proposition que l'on peut invertir, car pour ces dernières  $\Gamma$  (ou  $\Gamma^*$ ) l'ordre de la courbe double (ou la classe de l'enveloppe double) est deux; il faut donc qu'existent dix droites (ou points) singuliers, supposés tous de la première espèce. 8)

Entre ces  $\Gamma$  se trouve la Vôtre, caractérisée par la propriété d'avoir, en dehors des dix droites singulières  $B_i B_k, s_k$ , les quatre points singuliers  $B_i$ .

§ 5. J'ai donné, pour une telle  $\Gamma$ , la construction suivante: Soit  $\Delta$  une congruence de droites  $[7,2]$  de KUMMER, et soit  $\pi$  son plan singulier du 6<sup>me</sup> ordre. Faisons se correspondre sur  $\pi$  deux points lorsqu'ils sont les intersections avec  $\pi$  de deux droites de  $\Delta$ , telles qu'un plan focal

7) On désigne par  $C_M^4$  la quartique lieu des couples de  $\Gamma$  situés sur les droites issues de  $M$ . Voir note  $a$  § 1.

8) Voir note  $a$ , § 6.

de l'une et un de l'autre soient en faisceau avec  $\pi$ ; deux droites qui soient les intersections avec  $\pi$  des plans focaux d'une même droite de  $\Delta$ .

On obtient sur  $\pi$  deux correspondances  $\Gamma, \Gamma^*$ , associées entre elles: les traces sur  $\pi$  des dix plans singuliers du 3<sup>me</sup> ordre de  $\Delta$  sont droites singulières pour  $\Gamma$ , dont les couples de points sont conjugués par rapport à la conique  $a^2$ , suivant laquelle le plan  $\pi$  touche la surface focale de  $\Delta$ <sup>9)</sup>.

§ 6. Voici comment on peut spécialiser cette construction pour obtenir Votre correspondance.

Soit  $F^4$  une surface de STEINER; soient  $O$  son point triple,  $T$  le trièdre de ses droites doubles,  $Q$  le tétraèdre des plans qui la touchent suivant des coniques.

Sur un plan  $\pi$ , qui ne passe pas par  $O$ , les projections faites de  $O$ , des sommets de  $Q$  et les traces des faces de  $T$  sont les sommets  $B$ ; d'un quadrangle ( $B$ ) et les côtés de son triangle diagonal  $t$ .

Alors il y a sur  $\pi$  une transformation quadratique  $\Omega$ , dont  $t$  est le triangle fondamental et les sommets de ( $B$ ) sont les points doubles.

On rapporte à chaque point  $M$  de  $F^4$  le point  $M_1$  de  $\pi$ , correspondant en  $\Omega$  à la projection  $M_0$  de  $M$ , faite de  $O$  sur  $\pi$ .

On obtient ainsi une représentation biunivoque bien connue  $\rho$ , de  $F^4$  sur  $\pi$ ; les trois sommets de  $t$  sont l'image du point  $O$ , et les quatre sommets  $B_i$  de ( $B$ ) sont les images des quatre points de  $F^4$  alignés avec  $O$  et les sommets de  $Q$ .

Les droites telles que  $MM_1$  forment alors une congruence [7.2],  $\Delta$ , dont  $\pi$  est le plan singulier du 6<sup>me</sup> ordre, tandis que six de ses plans singuliers du 3<sup>me</sup> ordre sont ceux qui projectent de  $O$  les côtés du quadrangle ( $B$ ); en effet chacun d'eux,  $B_i B_k$ , — transformé en soi-même par  $\Omega$  — est l'image de la conique de  $F^4$  qui est dans le plan  $O B_i B_k$ ; ce plan contient, donc, la courbe de la 3<sup>me</sup> classe, enveloppée par les droites de  $\Delta$ , qui unissent les points de la conique à leurs images sur la  $B_i B_k$ ; il est, donc, un plan singulier du 3<sup>me</sup> ordre de  $\Delta$ .

Et alors, en construisant sur  $\pi$  les  $\Gamma, \Gamma^*$  de la manière exposée, six des dix droites singulières seront les  $B_i B_k$ , tandis que les quatre points  $B_i$ , par chacun desquels passent trois droites singulières, seront aussi singuliers; ce que précisément caractérise Votre correspondance.

§ 7. Voici, enfin, la construction de chaque  $\Gamma$  résultante de couples de points conjugués par rapport à une conique, que je désire de Vous signaler.

Étant données, dans le plan, la conique  $a^2$ , et une involution du 2<sup>me</sup> ordre et de la première classe,  $I^2$ , (il s'agira, dans le cas le plus général, d'une involution de GEISER, engendrée par un réseau de cubiques, avec sept points fondamentaux), il y a, sur chaque droite  $r$  du plan, un couple  $g$  de points conjugués par rapport à  $a^2$  et séparés harmoniquement par

<sup>9)</sup> Voir les § 3, 4, 5 de ma Note *b*, où la construction se rapporte particulièrement au cas dualiste.

le couple de  $I^2$  situé sur la droite  $r$ . Les couples  $g$  ainsi obtenus engendrent la  $\Gamma$ .

En effet, les couples de points de  $I^2$  alignés avec un point  $M$  forment une cubique  $C_M^3$ , passant par  $M$ ; la conique polaire de  $M$  par rapport à  $C_M^3$  et la droite polaire de  $M$  par rapport à  $a^2$  se coupent en deux points; c'est à dire que chaque point du plan appartient à deux couples  $g$ , tandis qu'une droite quelconque contient un couple  $g$ . Les couples  $g$  engendrent donc une  $\Gamma$ .

On obtient tout de suite les dix droites singulières de  $\Gamma$ ; en effet la transformée de la conique  $a^2$  au moyen de  $I^2$  est une courbe du 8<sup>me</sup> ordre, qui coupe  $a^2$ , en dehors des douze points qui sont aussi sur la courbe double de  $I^2$ , en dix couples de points de  $I^2$ ; les dix droites qui unissent les deux points de chaque couple sont les dix droites singulières de  $\Gamma$ .

§ 8. La construction indiquée est valable pour toute  $\Gamma$  résultant de couples de points conjugués par rapport à une conique  $a^2$ ; en effet, étant donnée une telle  $\Gamma$ , soit  $r$  une de ses droites singulières. Les couples de  $\Gamma$  situés sur les droites issues d'un point  $M$  de  $r$  engendrent une cubique  $C_M^3$ , passant par  $M$ ; et les quatre points de contact de la cubique  $C_M^3$  avec ses tangentes issues de  $M$  sont sur  $a^2$ ; tandis que  $M$  varie sur  $r$ , le groupe des quatre points varie sur  $a^2$ , et décrit une série  $g_4^1$ ; on peut, donc, obtenir sur  $a^2$  les groupes de cette série au moyen des coniques d'un faisceau  $(f)$ , qui ne contient pas la conique  $a^2$ ; le faisceau  $(f)$  sera projectivement rapporté aux points de la  $r$ , à chaque point  $M$  de  $r$  correspondra précisément la conique de  $(f)$  qui contient les quatre points de contact de la cubique  $C_M^3$  avec ses tangentes issues de  $M$ .

Or, si l'on coupe chaque conique de  $(f)$  par les droites issues du point correspondant  $M$  sur  $r$ , on obtient les couples d'une involution plane de la première classe  $I^2$ , dont les points fondamentaux sont les quatre points-base de  $(f)$  et les trois points de  $r$  qui appartiennent à la conique de  $(f)$  correspondante.

Le couple de  $I^2$  et le couple de  $\Gamma$ , situés sur une même droite  $x$  se divisent harmoniquement; en effet la conique de  $(f)$ , correspondant au point  $M$  commun aux droites  $r, x$ , contient les quatre points de contact de la cubique  $C_M^3$  avec ses tangentes issues de  $M$ ; elle est donc coupée par chaque droite qui passe par  $M$  suivant un couple de points (de  $I^2$ ) qui divise harmoniquement le couple déterminé par la même droite, en dehors de  $M$ , sur la  $C_M^3$ . On peut donc construire la  $\Gamma$  de la manière indiquée.

§ 9. Votre correspondance peut donc aussi s'obtenir au moyen de la même construction; il suffit de choisir, comme involution  $I^2$ , celle que l'on obtient en faisant correspondre entre eux deux points, lorsqu'ils sont les points de contact d'une droite du plan avec des coniques du faisceau  $(b^2)$ ; les sommets et les points diagonaux du quadrangle  $(B)$  seront, alors, les points fondamentaux de la  $I^2$ .

**Botany.** — "*The influence of temperature on protoplasmic streaming of Characeae*". By M. HILLE RIS LAMBERS. (Communicated by Prof. F. A. F. C. WENT.)

(Communicated at the meeting of February 28, 1925).

Although there is much literature about the influence of temperature on protoplasmic streaming in general — several researches dealing almost exclusively with the subject — yet the information nearly always proves to be qualitative. With regard to purely quantitative information on the contrary, one is almost entirely confined to the now rather old data of NÄGELI and VELTEN. Therefore it seemed desirable to study once more the influence of temperature, the more so because there is an apparent difference between the results of these two investigators. A short statement of the outcome of former workers will be given here, followed by a preliminary communication of the method used in this research and some results obtained.

In 1860 NÄGELI<sup>1)</sup> published his experiments with *Nitella syncarpa*, dating from as early as 1849. Therein he only mentions the lengths of time used by particles of the protoplasm in covering a certain distance, at temperatures from 0° to 37° C. He states that no streaming was to be seen at 0° C. and that it stopped — and quite suddenly — when he got beyond 37° C.

VELTEN<sup>2)</sup> experimented with *Chara foetida* among other plants. He, too, merely mentions lengths of time, and from his observations drew quite wrong conclusions about the increasing of velocity, as NÄGELI did before. At 0° C. he found streaming extremely slow, at about 42° C. "Wärme-starre" followed.

If one converts those periods of time into velocities as SCHAEFER<sup>3)</sup> did, the difference between the temperature-velocity relation according to the data of NÄGELI and those of VELTEN, shows clearly.

By constructing a graph from the converted values of NÄGELI and the corresponding temperatures, we obtain an evidently logarithmical curve; from those of VELTEN an irregularly broken "straight" line, sharply turning down above 39° C.

<sup>1)</sup> CARL NÄGELI. Ortsbewegungen der Pflanzenzellen und ihrer Theile. Beitr. zur wiss. Bot. Heft II 1860, p. 77.

<sup>2)</sup> W. VELTEN. Die Einwirkung der Temperatur auf die Protoplasmabewegung. Flora 59, 1876, p. 209.

<sup>3)</sup> K. L. SCHAEFER. Zur Lehre von der Reaktion des Protoplasmas auf thermische Reize. Flora 85, 1898, p. 135.

A "modern" work on protoplasmic streaming was written by EWART<sup>1)</sup>, who made a close and profound study of the temperature problem in which he traced too the influence of the timefactor: In his chapter "The influence of temperature" he gives data of *Chara foetida* and *Nitella syncarpa*, but merely at temperatures upward from 20° C. and 25° C. respectively, the temperature intervals being rather large. By converting his figures for harmless temperatures, an almost linear relation between temperature and velocity of streaming was obtained. In the discussion of my own results, I shall return to this point.

It proved desirable to construct a new apparatus for this investigation; as neither those used by the before mentioned authors nor those described elsewhere in literature (see COHEN STUART<sup>2)</sup>) seemed to answer the required purposes, which were:

*Any temperature should be easily kept constant within narrow limits.*

*It should be possible to obtain a higher or lower temperature at any desired speed i.e., a few minutes should suffice.*

The apparatus drawn and described proved to answer the requirements fairly well. Water from the tap, having streamed so long that a constant minimum temperature has been reached (in summer about 12.5° C., in winter about 10° C. in this laboratory) is carried under constant pressure through a tube immersed in boiling water. Now different constant temperatures may be obtained by regulating the quantity of water flowing through this tube<sup>3)</sup>.

From cock *A* tap water of the minimum temperature flows via tube *B* into the vessel *C*, hanging about 3 M. above the work table. Into this vessel also opens a wide tube *D* and a tube *E* of about the same proportions as *B*. In a time-unit more water flows in from *A* than may flow out through *E*. So the water level in *C* rises, and finally the water streams away through *D* too. The water flowing through *E* is now under constant pressure. By raising or lowering *E* with a rope over pulley *M*, this pressure may be varied.

The water streaming through *E* passes a tap *F*, the opening of which may be adjusted by means of a micrometer screw — speed 1 mm. The screwhead is a disk with 100 divisions so that it is possible to vary the taphole 10, if need be, 5  $\mu$ . Via this tap a regulated quantity of water flows through the tube *G* running through vessel *H*, in which the water is kept boiling rapidly by means of two Bunsen gas burners. The water quantity amounts

1) A. J. EWART. On the Physics and Physiology of Protoplasmic Streaming in Plants. Oxford 1903.

2) C. P. COHEN STUART. Ein Mikrothermostat zum Studium der Protoplasmaströmung. Rec. d. trav. bot. néerl. Vol. XIX, 1922 p. 139.

3) I am greatly indebted to Mr. P. A. DE BOUTER, mechanic at the Botanical Laboratory for the care and attention he gave to the finishing of the apparatus. Many difficulties were solved by his clear insight.



to a little more than  $\frac{1}{3}$  of the volume of *H*. The original quantity is kept constant by an open condensation-tube, fed by a fourth tube (not specified in the figure) coming from the vessel *C*. Except the bottom, *H* is totally isolated by a thick asbestos layer. A thermometer, gauge glass, and a screen around the gas burners need, perhaps, no further explanation.

Out of vessel *C* the now heated water flows into *J*, a somewhat boat-shaped little tank, that contains the object. In a vessel shaped in that manner there occurs no streaming of water of different temperatures, as has been proved.

Isolation was not necessary as the fall of temperature between entrance and exit proved to be extremely small, even at the highest temperatures. The object lies in a special objectroom made so that the water can pass through it, as has been demonstrated by filling the objectroom with Indian ink, which was quickly diluted and then disappeared entirely.

A section was removed from the metal bottom of *J*; under this a thick glass plate was attached. *I* lies about 3 mm higher on the remaining edge of the former bottom (not visible in longitudinal section).

The temperature of the object is measured by a very accurate quick-silver thermometer *N* divided into  $0.1^{\circ}$  C. The small bulb is placed as near as possible to the object. In order to protect the object, no strong objectives were used — always a carefully varnished objective III of LEITZ, combined with a compensation ocular 18 of ZEISS. In this way a quite efficient enlargement was obtained. The influence of the room temperature on the constancy of the temperature in *J* was particularly small. Direct sunlight has, however, been troublesome sometimes. In general, the temperature remained quite constant in the evening; therefore most observations were made then.

With this apparatus every desired temperature between about  $15^{\circ}$  C. (minimum temp. with widest opening of *F*) and about  $55^{\circ}$  C. may be obtained.

By tracing experimentally the temperatures corresponding to different positions of the screw and using a sufficient number of observations, one can construct the screw position-temperature curve, in order to interpolate from it the screw position for any desired temperature. This graph shows an asymptotic progress to both axes.

Temperatures under the minimum temperature of the tap water were obtained by siphoning ice water from a large tank containing broken ice. The velocity of streaming was regulated with a screw as *F*, the temperature of the water in *J* again quite depending upon the position of the screw. In this case the room temperature functioned as a practically constant heat source. In this way a temperature as low as  $0.6^{\circ}$  C. could be obtained.

Here, too, the different temperatures remained constant, because the room temperature, in absence of direct sunlight, varied very little or at any rate, very slowly.

The Characeae are still to be considered the standard material for all

investigations on protoplasmic streaming. They may be cultivated rather easily during the whole year so one never needs to be without material. *Chara foetida* A. Br., *Nitella mucronata* A Br. and *Tolypella prolifera* Leonh. were used in this research. For the material of the last two species I am indebted to the kindness of Prof. Dr. J. C. SCHOUTE, who sent a large supply to me.

*Nitella* always proved the best object. Here the observation is not hindered by the development of cortex cells and the incrustation of Calcium carbonate, as is so often the case with the genus *Chara*.

In measuring, the usual method was followed. A net-ocular micrometer was put into ocular 18. With the enlargement used here, 10 divisions of the micrometer marked a distance of 555  $\mu$ . The time needed for a particle of the protoplasm to pass a distance of 10 divisions was measured. For each temperature 5 to 10 measurements were recorded, of which an average was taken. Time was measured by a stopwatch correct to 0.1 sec.

It would carry us too far to enter here into the many difficulties that may occur with such measurements. I will only draw the attention to a method of measuring yielding good results in cases in which the statistical method could not be used. In very young Characeae cells a regular rotating protoplasmic layer is seen, sometimes of a considerable thickness. All particles lying in that stream, big ones as well as small ones, are carried off with an equal velocity. Now it turned out that when a certain particle was followed, its rotation time had a constant value with constant temperature, besides being independent to its size. Especially at high temperatures at which the influence of the time factor was observed, this method was to be preferred to the usual one, each rotation being an expression of the velocity of the whole protoplasm.

Usually it was necessary to use a 100 candle lamp when making observ-

TABLE I  
Februari 12<sup>th</sup> 1925. Whorlcell of *Nitella mucronata* A Br.

Temperature.	Time in 0.1 sec for 10 div. net-oc. Micr. = 555 $\mu$ .									
29.7° (1)	62	58	62	63	62	59	58	60	61	58
23.6° (2)	79	79	77	78	77					
21.3° (3)	88	87	86	85	85	86	85	85	83	85
19.1° (4)	97	97	99	97	95					
29.5° (5)	61	62	60	59	61					
32.3° (6)	54	52	53	53	54					
34.1° (7)	49	51	49	51	50					
22.1° (8)	83	85	80	81	82	82				

ations. No damaging effect of this light could be observed. The distance between the lamp and the mirror of the microscope was usually about 30 cm. The influence of radiating heat is certainly excluded by the streaming water. A young terminal shoot of *Nitella*, exposed to this lamp light 24 hours at a time, in an object room  $L^1$ ) showed acceleration of streaming but no injury whatever, in spite of the lamp being quite near the microscope.

In Table 1 the lengths of time of the first eight observations are given, the converted values of which may be found in the curve of Fig. 2.

In starting and stopping the watch a mistake amounting to 0.2 sec. for each measurement may be made, that is not easily taken into account.

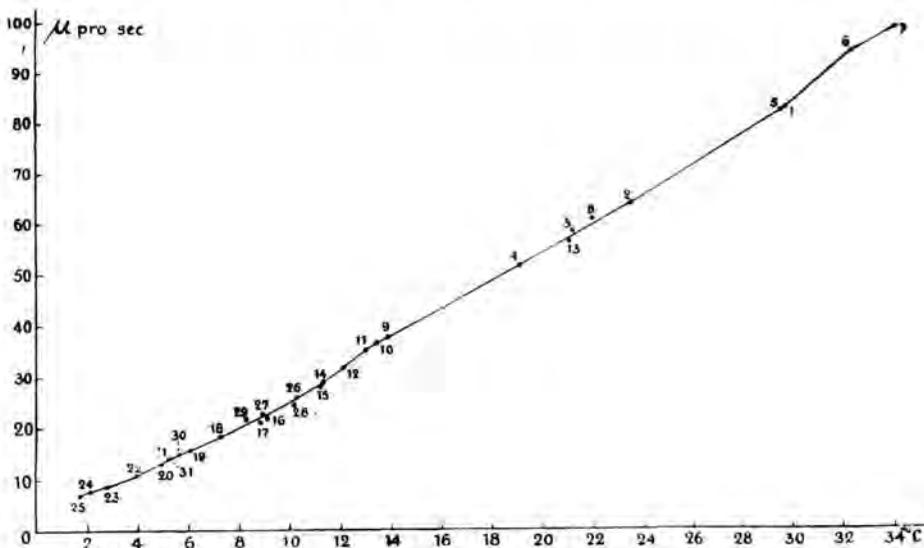


Fig. 2.

The curve in Fig. 2 refers to a whorlcell of *Nitella mucronata*. As in most experiments, here, too, the apical end of a young shoot was used. The numbers 1 to 31 at the dots of the curve, mark the order of the observations. One can see that the velocity data are reproducible, no difference of velocity being caused by the order in which the different temperatures act upon the object.

Sometimes the phenomenon of "shock" occurs when suddenly passing from a very high temperature to a very low one; streaming stops quite suddenly, and not until 10 to 20 min. afterwards is the velocity corresponding to the temperature attained. If no shock follows by changing the temperature, then the velocity of streaming adjusts itself always quite normally. The curve of Fig. 2 is typical for all Characeae I have observed until now. The conformity is so strong that *Chara*, *Nitella* and *Tolypella* at the same temperature often show velocities that are almost equal and

<sup>1)</sup>  $L$  was placed on the stage of the microscope. Here the acceleration of streaming was an heat effect.

sometimes are even quite the same. The curve often approaches a straight line, at least the part that contains the values above 14° C. By using short heating times (which is allowed with these objects under the mentioned circumstances, because another temperature and the corresponding velocity also, is almost immediately assumed) I could prove a few times that the temperature velocity curve continued its typical progress as far as 39° C. However, I have reason to believe that the velocity curve of the protoplasm itself will have slightly higher values than those got by measuring the particles carried off by the stream. Also the time factor may lower the velocities obtained above 30° C., a question into which I shall not now enter.

My own results, compared with those of NÄGELI and VELTEN, resemble for the greater part those of the later. How NÄGELI got a logarithmical curve so strongly bent is quite unintelligible to me. On the whole, the progress of this and other curves reminds one very strongly of fluidity graphs. ( fluidity =  $\frac{1}{\text{viscosity}}$  ).

EWART (p. 120 l.c.), too, states in his "summary of results", "As the temperature rises within certain limits the viscosity decreases, and a large part of the increased velocity of streaming is due to this cause alone".

I, no more than EWART, want to deny the existence of other factors, but I am convinced that the *visible* and *measurable* result of the influence of temperature is due to change of viscosity.

*Botanical Laboratory.*

*Utrecht, February 1925.*

**Chemistry.** — *"The Metastability of the Elements and Chemical Compounds as a Consequence of Enantiotropy or Monotropy"* IX.  
By Prof. ERNST COHEN and Dr. A. L. TH. MOESVELD.

(Communicated at the meeting of November 29, 1924).

1. In a series of investigations, published<sup>1)</sup> under the above title with BRUINS, HELDERMAN, and KOOY, we have called attention to, and qualitatively and quantitatively proved, the fact, that the physical constants of the substances which have been determined up to this time, often refer to metastable mixtures of unknown composition of the modifications of those substances, so that no significance whatever can be attributed to those, quite fortuitous, values. Only then do they get any significance when those constants are determined for the pure modifications. In the case of cadmium iodide and ammonium nitrate respectively, we have already proved, that this may lead to errors of f.i. 5 and 9<sup>0</sup>/<sub>0</sub>, but in certain cases much greater errors are also possible<sup>2)</sup>.

In the course of this paper we wish to draw attention to two new cases which again indicate the absolute necessity of ascertaining that, in determining physical constants of solid substances, the pure modifications of the substance we wish to investigate are actually used, as otherwise absolutely valueless results are obtained.

The cases to be treated here refer to the determination of the specific heats of white (tetragonal), and grey tin, at temperatures lying between +18° C. and the absolute zero, as well as the determination of the heat of transition of those modifications.

In the first place we point to the fact, that in our previous investigations<sup>3)</sup> we proved that these two modifications are enantiotropic, with the proviso, that grey tin is stable below the transition temperature of +18° C., and white tin above this temperature. The phenomena

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<sup>1)</sup> Zeitschr. f. physik. Chemie **94**, 450, 465, 471 (1920); **109**, 81, 97, 100, 109 (1924); **113**, 145 (1924).

<sup>2)</sup> The magnetic susceptibility of grey tin, according to the investigations by HONDA is different from that of white tin, not only in sign, but more than ten times as great. The presence of only a few per cent of one modification by the side of the other would, in this case, lead to very important errors.

<sup>3)</sup> Zeitschr. f. physik. Chemie **30**, 601 (1899); **33**, 57 (1900); **35**, 588 (1900); **48**, 243 (1904); **50**, 225 (1905); **53**, 625 (1908); **68**, 214 (1909).

of retardation in the transition of the white into the grey modification, however are so persistent, that down to very low temperatures the white tin can remain in a metastable state. It is owing to this fact that the phenomenon of stabilization at a low temperature (the transition from the white state into the grey, tin disease) has been discovered only in recent times.

2. It is true that in a previous paper we indicated, how it was possible to greatly accelerate stabilization, (adding germs of grey tin, as well as a solution of an electrolyte, at temperatures below the transition point, while at the same time we must take into consideration, that there is an optimum temperature for stabilization, *which depends on the previous history of the material*), by which means it has become possible to prepare unlimited quantities of grey tin in no long time (days, weeks), but we have been careful not to give the physical constants of grey tin, such as density, specific heat, heat of transition, etc. because our investigations in this direction, had never been made in such a way, that we were sure of having the absolutely pure grey modification. In agreement with this we wrote, after concluding this part of our investigations, in ABEGG's Handbuch der anorganischen Chemie<sup>1)</sup>:

"Graues Zinn. Das spez. Gewicht dieser Modifikation ist bisher nicht genau ermittelt worden; die Messungen von SCHERTEL, RAMMELBERG, HJELT und STOCKMEIER beziehen sich alle auf Gemische von grauem und weissem Zinn, doch dürfte es in der Nähe von 5.8 bei 15° C. liegen". And further: "Dem von BUNSEN ermittelten Werte für die spezifische Wärme des grauen Zinns (er fand dafür 0.0545) kann eine Bedeutung nicht beigelegt werden, da das von ihm untersuchte Präparat offenbar ein Gemenge von weissem (tetragonalem) und grauem Zinn gewesen ist".

If it is not certain, that the material to be investigated is composed of a single, pure modification, the determination of physical constants is of course without any value whatever.

3. It is often difficult to prepare such a pure material, and this is especially the case with tin, where the retardations in the stabilization are so very persistent. Neither is it easy in such a case to find a sharp criterion which demonstrates that the transition in the desired modification has completely occurred. Consequently the proof will be found in this paper that up to the present the preparing of a preparation of grey tin, answering to the requirements that ought to be fulfilled, has not been successful.

4. During the last twelve years more than one investigator has tried to determine accurately the specific heats of the two modifications of tin

<sup>1)</sup> Vol. 3, (2) 556 (1909), Leipsic.

which we are discussing here: WIGAND <sup>1)</sup>, BRÖNSTED <sup>2)</sup>, and of late LANGE <sup>3)</sup> have occupied themselves with this problem.

We need not enter into the first investigation of WIGAND <sup>1)</sup>, as he himself has withdrawn the results he then obtained.

But the second communication by WIGAND is of no importance to us either, if we adopt the standpoint that we may only expect reliable results, if the *chemical* purity of the material used answers the necessary requirements. Now WIGAND himself says however: "Eine Untersuchung der Präparate auf ihren Gehalt an reinem Zinn wurde unterlassen, da es im wesentlichen nur auf das Vorzeichen der Differenz der spezifischen Wärmen beider Modifikationen ankam".

5. BRÖNSTED writes as follows about his material, used in determining the mean specific heats between 0 and 19°.00 C. and about the results he obtained:

1. *Weisses (tetragonales) Zinn*. Reinstes Metall von KAHLBAUM bezogen: 0.05386; 0.05383; 0.05379; 0.05374; 0.05389, Mittel 0.05382.

2. *Graues Zinn*. Aus dem benutzten reinen weissen Zinn bei  $\div$  20° hergestellt, ohne Anwendung eines Lösungsmittels:

0.04950; 0.04972; 0.04971; 0.4964; 0.04951, Mittel 0.04962.

Als Differenz ergibt sich hier  $c_w - c_p = 0.00420$ .

3. *Weisses Zinn*. Aus dem in Versuch 4 angewandten grauen Zinn bei  $\frac{1}{2}$  stündigen Erhitzen auf 80° dargestellt:

0.05481; 0.05473; 0.05466, Mittel 0.05473.

4. *Graues Zinn*. Dieses Präparat wurde aus geraspelttem weissem Zinn mittels alkoholischer Pinksalzlösung bei  $\div$  20° dargestellt:

0.05056; 0.05056; 0.05065, Mittel 0.05059.

Wir sehen, dass die unter den Abschnitten 3 und 4 angeführten Werte etwas höher sind, als die zuerst angeführten, was leicht zu erklären ist. Bei der Behandlung mit der alkoholischen Salzlösung wird ein Teil des Metalles oxydiert, wodurch eine Erhöhung der spezifischen Wärme stattfindet. Die Differenz der spezifischen Wärmen wird dadurch nur sehr wenig beeinflusst, da die Oxydmenge in den beiden Modifikationen dieselbe ist. Tatsächlich ergibt sich aus den Abschnitten 3 und 4:

$$c_w - c_p = 0.00414.$$

6. In his second investigation BRÖNSTED has determined the true specific heat of the two modifications at different temperatures between 79.8 and 288°.1 K.

<sup>1)</sup> Zeitschr. für Elektrochemie **20**, 38 (1914).

<sup>2)</sup> Zeitschr. für Elektrochemie **18**, 714 (1912); Zeitschr. f. physik. Chemie **88**, 479 (1914).

<sup>3)</sup> Zeitschr. f. physik. Chemie **110**, 343 (1924).

<sup>4)</sup> Marb. Ber. 1906, S. 196; Ann. der Phys. **22**, 64 (1907).

Table 1 contains the results obtained. From his paper we borrow the following data which are of importance for our further discussion:

„Als Kalorimeter diente bei meinen Versuchen ein Silbergefäß, das etwa 150 g. graues Zinn fassen konnte. Das Kalorimeter wurde zuerst mit grauem Zinn gefüllt und dann mit WOODSchem Metall luftdicht zugelötet. Wenn die Versuche mit der grauen Modifikation beendet waren, wurde das Kalorimeter mit Inhalt ungeöffnet eine Stunde auf 60° erhitzt, wobei die Umwandlung in weisses Zinn sich vollzieht. Das in dieser Weise hergestellte weisse Zinn war bei der Temperatur der flüssigen Luft vollkommen beständig, bei - 80° wandelte es sich aber langsam in graues Zinn um, so dass es hier nötig war nicht-umgewandeltes weisses Zinn zu verwenden. Bei Versuchen bei 0° und in flüssiger Luft zeigten sich die beiden Präparate von weissem Zinn identisch“.

As BRÖNSTED in his second paper does not give further data about his preparations of tin, we have asked him for information. He writes to us as follows: „In den beiden Arbeiten wurde reines Zinn in Stangen von KAHLBAUM benutzt. Soweit ich sehen kann, wurde in der zweiten Arbeit das graue Zinn frisch hergestellt; die Präparate waren also sicher nicht identisch, wenn auch von gleicher Provenienz“.

TABLE 1.  
Atomic heat ( $C_g$ ) of grey tin and ( $C_w$ ) of white tin  
(BRÖNSTED).

$T$	$c_w$ (exp.)	$c_g$ (exp.)
79.8	4.64	3.80
87.3	4.87	4.07
94.8	5.07	4.30
194.9	6.20	5.66
197.2	6.23	5.71
205.2	6.25	5.75
248.4	6.36	5.87
256.4	6.37	5.88
264.3	6.38	5.89
273.0	6.39	5.90
288.1	6.40	5.91

Mean values of about 40 single determinations (mean deviation about 1%).

7. We shall now occupy ourselves with LANGE's investigation, which was published a few months ago. He also determined the specific heats in question, in order to use the values obtained for thermodynamic calculations. His measurements of the true specific heats of the two modif-

ications are carried out in the temperature interval of  $9^{\circ}.60$  to  $286^{\circ}.3$  K.

As regards the preparations of white and grey tin used he only says in the paper above mentioned: "Das graue Zinn wurde nach den von COHEN gegebenen Vorschriften aus "Zinn KAHLBAUM" hergestellt", and further: "Zu den Messungen (am weissen Zinn) wurden 169.23 g. "Zinn KAHLBAUM" verwandt". We have asked Prof. BODENSTEIN at Berlin for further information, who wrote to us: "Das weisse Zinn ist in Form der von KAHLBAUM gelieferten Stangen benutzt worden; die sind dann geraspelt und nach Ihrer Vorschrift in Pinksalzlösung in graues verwandelt worden unter Verwendung von Keimen von einem Material, das aus dem hiesigen Laboratorium stammte und direkt zur Messung benutzt, unsinnige Werte ergeben hatte. Aus der Pinksalzlösung ist das graue Zinn abfiltriert, mit Alkohol gewaschen und im Vakuum getrocknet worden."

8. Table 2 contains the results of LANGE's measurements. He writes:

TABLE 2.  
Atomic heat of grey and white tin (LANGE).

Gray tin 67.49 g.		White tin			
		First series		Second series	
<i>T<sub>m</sub></i> .	<i>At. H.</i>	<i>T<sub>m</sub></i> .	<i>At. H.</i>	<i>T<sub>m</sub></i> .	<i>At. H.</i>
15.5	0.599	22.4	1.27	9.60	0.206
18.2	0.755	26.9	1.87	10.60	0.266
22.35	1.056	32.7	2.48	11.72	0.346
26.8	1.375	40.9	3.04	12.64	0.435
31.5	1.675	42.5	3.21	13.31	0.477
37.3	2.00	48.0	3.53		
44.9	2.36	56.7	4.06		
52.3	2.80	92.5	5.21		
59.3	3.14	101.1	5.40		
69.5	3.67	286.3	6.27		
92.5	4.42				
102.6	4.73				
283.7	6.13				

*T<sub>m</sub>* is the mean of initial and final temperature during the experiment, in absolute temperatures, while under *At. H.* the atomic heats are given.

“Die gefundenen Werte sind in beiden Fällen <sup>1)</sup> um einen nennenswerten Betrag verschieden gegenüber den BRÖNSTED'schen Messresultaten. Nun aber dürfen die hier mitgeteilten Werte vom weissen Zinn als sehr gesichert gelten, weil beide Messreihen (mit verschiedenen Apparaturen) gut an einander anschliessen und bei höheren Temperaturen eine gute Uebereinstimmung besteht sowohl mit den Messungen von BEHN als auch mit denen von JÄGER und DIESELHORST. Es ist also anzunehmen, dass die Messungen von BRÖNSTED durch einen systematischen Fehler entstellt sind”.

9. LANGE writes about the accuracy of the figures found for the specific heat: “Die Fehlergrenze bei der Bestimmung der auftretenden Temperaturdifferenzen dürfte bei tiefen Temperaturen etwa 1 ‰, oberhalb von 150 abs. 1.5 ‰ betragen, so dass entsprechend für die einzelnen spezifischen Wärmen ein Maximalfehler von etwa 1.5 bis 2 ‰ anzusetzen sein wird”.

10. We shall now inquire a little deeper into the investigations mentioned, and consider in how far they offer a guarantee that the preparations of grey and white tin used, indeed satisfy the requirements which ought to be attained in this case.

In BRÖNSTED's as well as in LANGE's researches we look in vain for any criterion, guaranteeing the *physical* purity of the substances. No indication whatever is given enabling us to deduce, that the stabilization into grey tin is in fact complete, neither with the grey tin (see above under 5) which is prepared without the solution of an electrolyte, nor with the preparation which was brought in contact with a solution of pink salt (see above par. 5 under 4). Moreover BRÖNSTED mentions in his second investigation (see above par. 6) a manipulation which leads us to suppose that the material he put into his silver calorimeter, was afterwards, partly at least, transformed into the white modification, even if before this manipulation it had consisted entirely of grey tin. For he solders up the calorimeter with WOOD's metal, an alloy, the melting point of which lies at 71°. Now the velocity of transition of grey tin into white is — as our former investigations <sup>2)</sup> have proved already very considerable <sup>3)</sup> at 35°, and as silver is the metal which, preeminently, conducts heat, the chance is very great that during soldering, the transformation has partly taken place. This is the reason that the values found for the specific heat of grey tin are doubtful.

11. But also as regards the determination of the specific heat of white tin, we remain in doubt, as it was not stated if that white

<sup>1)</sup> i.e. with the grey as well as with the white tin.

<sup>2)</sup> Zeitschr. f. physik. Chemie 33, 57 (1900).

<sup>3)</sup> Negative catalysers for this transition are not known up to the present.

tin, prepared from the grey, by heating it to 60° for one hour, had indeed been quantitatively transformed into the white modification. Nevertheless we think it probable that this has indeed been the case.

12. If we now turn to the investigation of LANGE, here also the question arises: what are we to think of the *physical* and *chemical* purity of the substances used?

It is certain that, on account of the method of preparation followed by LANGE, the grey tin was chemically contaminated, in consequence of contact with a solution of pink salt, which causes oxidation. In consequence of the presence of the  $\text{SnO}_2$  thus formed, the specific heat of the preparation will increase. But for the rest every criterion is wanting that the white tin has really been transformed into grey. So LANGE's measurements may also relate to mixtures of the two modifications, even putting aside the contamination by  $\text{SnO}_2$  which we mentioned above.

13. As LANGE found values for white tin at temperatures, at which BEHN as well as JÄGER and DIESELHORST also experimented, and his values do not deviate much from theirs, he is of opinion (see above par. 8), not only that these values are correct, but also that BRÖNSTED's measurements are affected with a systematic error. He overlooked the fact that the tin he used which was cast in bars, had not been tested for its *physical* purity, and that the same may be said of the material used by JÄGER and DIESELHORST. For the investigations of DEGENS <sup>1)</sup>, and by WERIGIN, LEWKOJEFF and TAMMANN <sup>2)</sup> as well as those of SMITS and DE LEEUW <sup>3)</sup>, and of WERNER <sup>4)</sup>, have taught that white tin has a second transition point, and that also at this transition (white, tetragonal tin  $\rightleftharpoons$  white, rhombic <sup>5)</sup> tin) very persistent retardations take place. As neither JÄGER and DIESELHORST, nor LANGE paid attention to this fact, we are uncertain about what happened with their tin, when the bars were cast (solidifying of the molten tin). So here too the guarantee for *physical* purity is wanting, and the value of these determinations is wholly fictitious.

14. From what precedes it is evident that we have no guarantee, that either the preparations of BRÖNSTED, grey and white (tetragonal) tin, or LANGE's have been *physically* pure. No significance therefore can be attached to the values of the specific heats of those modifications,

<sup>1)</sup> Zeitschr. f. anorg. Chemie **63**, 207 (1909).

<sup>2)</sup> Drudes Ann. **10**, 647 (1903).

<sup>3)</sup> These Proceedings **15**, p. 676 (1912).

<sup>4)</sup> Zeitschr. f. anorg. Chemie **83**, 275 (1913).

<sup>5)</sup> In connection with the communications of SPENCER Min. Magaz. **19**, 113 (1921) and of MÜGGE (Centralblatt Min. 1917 pag. 233) we shall not discuss the question whether the form, called rhombic here is rhombic indeed.

which, as it happens, are widely divergent; neither can any value be attached to the thermodynamic calculations, which are based on these figures.

15. As BRÖNSTED, when determining the heat of transition of grey into white (tetragonal) tin, also used a material which had not been checked, the value found for this heat effect also loses its significance.

The investigations treated in this paper, will have to be repeated with a material that is *chemically* as well as *physically* pure. We hope to revert to this subject at a later period.

#### SUMMARY.

The investigations carried out up to the present time, on the specific heats of grey and white (tetragonal) tin, as well as those made to determine the heat of transition of those modifications, prove again that it is absolutely necessary to be sure of the *chemical*, as well as of the *physical* purity of the substances to be investigated, before they can be used for determining physical constants.

*Utrecht*, November 1924.

VAN 'T HOFF-Laboratory.

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**Physics.** — “*On the Cohesive Forces of Liquids*”, By A. TH. VAN URK.  
(Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of March 28, 1925).

§ 1. *Introduction.*

In 1805 shortly after each other appeared the theories of YOUNG<sup>1)</sup> and LAPLACE<sup>2)</sup> on the cohesion of liquids, of which the latter has held its grounds up to now, whereas YOUNG's theory is almost forgotten.

In VAN DER WAALS's well-known thesis for the doctorate: „*On the Continuity of the Gaseous and the Liquid State*” we find YOUNG's name not even mentioned in the discussion of LAPLACE's theory, so that probably VAN DER WAALS did not know YOUNG's work. Yet YOUNG already gives an estimation of the internal pressure and of the distance of the elementary liquid atoms, and besides of the range over which the attractive force acts. It appears already here that YOUNG finds these two distances of the same order of magnitude. The same thing is also stated by VAN DER WAALS in the above-mentioned thesis for the doctorate.

An excellent survey of YOUNG's and LAPLACE's theories (the latter given according to MAXWELL) is to be found in RAYLEIGH, *Collected Papers*, Vol III, p. 396. It is unnecessary to repeat his calculations here; we will only mention some results:

$$K_0 = \frac{2\pi}{3} \int_0^{\infty} z^3 \varphi(z) dz \quad T_0 = \frac{\pi}{8} \int_0^{\infty} z^4 \varphi(z) dz.$$

In this  $K_0$  is the internal pressure, and  $T_0$  the surface tension  $z$  representing the distances of the molecules;  $\varphi(z)$  is a force, a function of  $z$ , which is insensible for all sensible values of  $z$ , but which becomes sensible and even enormously great, when  $z$  is exceedingly small.

As the simplest example of such a force RAYLEIGH gives  $\varphi(z) = e^{-\beta z}$ . This yields for the relation of  $T_0$  and  $K_0$ :  $T_0 = \frac{3}{4} \frac{1}{\beta} K_0$ . (The range of the force is of the order of magnitude  $\frac{1}{\beta}$ ).

As a second example RAYLEIGH takes  $\varphi(z) = z^n$ , and finds that for any value of  $n$ , whatever it may be, the internal pressure becomes infinite.

<sup>1)</sup> YOUNG. *On the cohesion of fluids*. *Phil. Trans.* 1805. Vol. II, p. 657.

<sup>2)</sup> LAPLACE, *Méc. Cél.* Tome IV, p. 399.

The cause of this lies in the fact that RAYLEIGH takes zero for the lower limit of integration, which is not allowed for other than point-molecules.

YOUNG himself gives  $T_0 = \frac{1}{3} a K_0 \left( a = \frac{1}{\beta} \right)$  as relation between  $T_0$  and  $K_0$ . RAYLEIGH, however, as result of the calculation according to YOUNG's supposition: i.e. an attractive force constant for the small distance over which it acts balanced by a repulsive force in inverse ratio to the distance,  $T_0 = \frac{3}{20} a K_0$ .

RAYLEIGH says about this difference in result: „The discrepancy seems to depend upon YOUNG having treated the attractive force as operative in one direction only”. I have not succeeded in seeing this part of YOUNG's work, hence I have not been able to form an opinion on this point.

Further VAN DER WAALS gives a theory on surface tension <sup>1)</sup>, in which he assumes  $-II(f) = \frac{Ae^{-f/\lambda}}{\lambda} \left( \lambda = a = \frac{1}{\beta} \right)$  as potential of the attractive forces. This assumption yields  $T_0 = \frac{1}{2} \lambda K_0$ . The coefficient  $1/2$  is in agreement with what STEFAN already expected for the ratio between the work required to bring a molecule at the surface and that required to bring a molecule quite outside the reach of the liquid fields of force when VAN DER WAALS's equation of state is valid. <sup>2)</sup>

Hence it appears from the results given that with a theory in which the forces vary continuously with the distance and reach many molecules far, widely divergent results are possible, dependent on the force function assumed.

Now it has, however, already appeared from VAN DER WAALS's and YOUNG's estimations that the attractive forces operate over distances comparable with the diameter of the molecules, and in „Bemerkung zu dem Gesetz von EÖTVÖS” <sup>3)</sup> also EINSTEIN arrives by a theoretical way at the result that the attractive forces act only between molecules lying immediately side by side.

The direct experimental proof has finally been furnished by LANGMUIR's researches on mono-molecular liquid films <sup>4)</sup>. They form the conclusion of a long series of researches starting with Miss POCKELS and RAYLEIGH. They seem to have been prompted by a remark of MAXWELL in the Scientific Papers Vol. II p. 549, viz:

“The phenomenon of very thin liquid films deserve the most careful

<sup>1)</sup> v. D. WAALS—KOHNSTAMM 1<sup>er</sup> Teil p. 208.

<sup>2)</sup> WIEDEM. Ann. Bd. 29. p. 655, 1886. Compare also KUENEN: Die Eigenschaften der Gase Kap. 14. p. 380, et seq..

<sup>3)</sup> Ann. der Physik 1911. Bd. 34.

<sup>4)</sup> Journ. of the Am. Chem. Soc. Vol. 38. Nov. and Vol. 39. Sept.

study, for it is in this way that we are most likely to obtain evidence by which we may test the theories of the molecular structure of liquids".

It seems desirable to me to calculate the internal pressure and the surface tension with such forces, the more so where it is possible to test the results by experimental data. So far it has been only rarely tried to compare the relations between  $T_0$  and  $K_0$  with the data. I am only acquainted with the comparison by EINSTEIN (loc. cit.) for benzene and mercury, and VAN LAAR's computations in the *Chemisch Weekblad* of 1918 and 1919. He tries to show via VAN DER WAALS'S a that RAYLEIGH'S recorded result  $^{3/20}$  conforms about to reality for so-called normal (i. e. non-associating substances. In what follows a relation will be drawn up for *simple* gases and examined for them, in contrast with LANGMUIR, who has always worked with very complicated organic substances.

### § 2. Calculation of the formulae.

Following LANGMUIR we shall suppose that the forces are specific: i. e. entirely determined by the molecule from which they start; operating in definite directions;

that their range is restricted to the molecules lying nearest;

that the number of molecules that can enter into interaction with a definite molecule is entirely controlled by the number of directions of force issuing from the molecules.

We now get the following image of a liquid:

Every molecule has a same number of directions of force along which the forces act through which the molecules are connected with each other, and which we shall call rods in what follows. If we now suppose the liquid without heat motion, hence cooled down to the absolute zero point, but remaining liquid and not crystallized (i. e. without particular structure), we can calculate  $T_0$  and  $K_0$  accurately; at least if all the rods have the same length and are equally strong. In this case we shall assume the substance in the solid state to be regular. In the calculation we shall make use of the property that internal pressure and internal heat of evaporation per ccm. are represented by the same number. (See RAYLEIGH, loc. cit. p. 421).

If we now take a cube of liquid of 1 ccm., containing  $N$  molecules, and if every molecule possesses  $k$  rods, the total number of rods per unit volume is  $\frac{Nk}{2}$ .

If we call the work required to break one rod,  $s$ , the total work to break all the rods, hence the internal heat of evaporation is  $\frac{Nks}{2}$ .

To calculate the surface tension we may proceed as follows: we take a plane, parallel to the plane of the cube, and calculate how many rods intersect this plane. The work required to break the cube according to this plane is equal to twice the surface tension. The rods will now have

all possible orientations in the liquid. The number of rods that form an angle between  $\theta$  and  $\theta + d\theta$  with the normal to the plane considered is  $\frac{Nk}{2} \cdot \frac{2\pi \sin \theta d\theta}{4\pi}$  per unit of volume. Let all the rods have the same length  $l$ , rods forming an angle  $\theta$  with the normal, will still just intersect the plane, if they lie in the parallelepiped that adjoins the plane and has a height equal to  $l \cos \theta$ . This holds for both sides of the plane, and as  $\theta$  can vary from 0 to  $\frac{\pi}{2}$  the total number of rods intersecting the plane is:

$$\int_0^{\pi/2} \frac{Nk}{2} \cdot \frac{2\pi \sin \theta d\theta}{4\pi} \cdot l \cos \theta \cdot 2 = \frac{Nkl}{2} \int_0^{\pi/2} \sin \theta \cos \theta d\theta = \frac{Nkl}{4} \sin^2 \theta \Big|_0^{\pi/2} = \frac{Nkl}{4}$$

Hence the surface tension is  $\frac{Nkls}{8}$ .

We find for the relation of  $T_0$  and  $K_0$ :

$$\frac{2 Nkls}{8 Nks} = \frac{l}{4} \text{ hence } T_0 = \frac{1}{4} l K_0 \dots \dots \dots (1)$$

For the numerical calculation it is convenient to transform this formula somewhat. Multiply left and right by  $\left(\frac{M}{d} \cdot \frac{1}{N}\right)^{2/3}$ , then we may write:

$$\left(\frac{M}{d} \cdot \frac{1}{N}\right)^{2/3} \cdot T_0 = \frac{1}{4} \cdot \left(\frac{M}{d} \cdot \frac{1}{N}\right) K_0 \cdot \frac{l}{\left(\frac{M}{d} \cdot \frac{1}{N}\right)} \dots \dots \dots (2)$$

Now  $\frac{M}{d}$  is the number of ccm. per gr. mol., hence  $\frac{M}{d} \cdot \frac{1}{N}$  the vol. per molecule in ccm., and  $\frac{M}{d} \cdot \frac{1}{N} \cdot K_0$  is the work for the vol. of a molecule, hence required to detach a molecule.  $\left(\frac{M}{d}\right)^{2/3} T_0$  is the molecular surface tension.

We must finally make some conclusion about the length of the rods and the number of molecules in a surface of the cube that contains a gramme-molecule. In what follows  $N^{2/3}$  has been assumed for the required number, and  $\left(\frac{M}{d} \cdot \frac{1}{N}\right)^{1/3}$  for the length, i. e. the side of a cube occupying the same volume as is available for a molecule. If it is, however, assumed that the molecules fill the volumes as spheres packed as closely together as possible, the length would have to be  $l_1 = 1,12 l$ . Instead of  $\frac{1}{4}$  the constant of the formula would then have become 0,28.

Recapitulating we see that the lefthand member of equation (2) represents the mean surface tension per molecule  $\sigma_0$ , and the righthand member without the coefficient  $\frac{1}{4}$  the mean internal heat of evaporation per molecule  $L_0$ , both at the absolute zero. Hence formula (2) becomes:

$$\sigma_0 = \frac{1}{4} L_0 \quad \dots \dots \dots (3)$$

§ 3. *Testing by the data.*

For the surface tension there are available BALY and DONNAN's measurements on hydrogen, nitrogen, and argon <sup>1)</sup>, and those of KAMERLINGH ONNES and KUYPERS on hydrogen <sup>2)</sup>.

On the heat of evaporation of the same substances publications have appeared by MATHIAS, CROMMELIN, and KAMERLINGH ONNES <sup>3)</sup>. To obtain the  $\sigma_0$  from formula (3) it is sufficient to put  $T=0$  in the formula for the molecular surface tension of BALY and DONNAN, and divide by  $N^{2/3}$ . The internal heat of evaporation is obtained by diminishing the values of the heat of evaporation with the external work; the values found thus were plotted on a large scale, and then extrapolated linearly to  $T=0$ . For greater certainty in this graphical representation also the values of the heat of evaporation itself were plotted, to see if the heat of evaporation goes to the same point on extrapolation.

We now multiply these values by the molecular weight and the mechanical equivalent of heat, and divide by  $N$ . We get the internal heat of evaporation in ergs per molecule at  $T=0$ , hence the  $L_0$  from the righthand member of equation (3).

Of the four substances given hydrogen is regular, probably triakis- or hexakis-octahedral, argon and nitrogen regular at the melting-point, and oxygen hexagonal at the melting-point according to visual observations by W. WAHL <sup>4)</sup>. This has since been confirmed by Röntgenograms at Leiden and Berlin.

We shall give the data below.

Constants used:

$N$  (number of mol. per gramme-mol.)  $6.062 \cdot 10^{23}$ .

Mech. equivalent of heat  $4.189 \cdot 10^7$ .

Molecular weights: hydrogen 2.016, argon 39.9, nitrogen 28.00 and oxygen 36.00.

Molecular surface tensions:

Hydrogen:  $\sigma = 1.294 (34.49 - T)$  <sup>5)</sup>.

<sup>1)</sup> Journ. of the Chem. Soc. 81, pg. 907. 1902.

<sup>2)</sup> Leiden Comm. N<sup>o</sup>. 142d.

<sup>3)</sup> Leiden Comm. N<sup>o</sup>. 162.

<sup>4)</sup> W. WAHL. Zeits. für phys. chem. Bd. 84. 1913 p. 101.

<sup>5)</sup> This formula has been calculated from KAMERLINGH ONNES' and KUYPERS' observations.

Argon:  $\sigma = 2.02 (145.44 - T)$ .

Nitrogen:  $\sigma = 2.002 (124.29 - T)$ .

Oxygen:  $\sigma = 1.917 (153.77 - T)$ .

Heats of evaporation:

Hydrogen				Nitrogen			
$T$	$L$ (gr. cal.)	$W$	$L_i$	$T$	$L$ (gr. cal.)	$W$	$L_i$
32.52	35.40	8.11	27.3	125.01	9.17	2.04	7.13
31.26	58.14	12.26	45.9	124.48	11.40	2.33	9.07
30.06	71.44	14.26	57.2	123.34	15.03	2.82	12.21
28.79	81.45	16.62	64.8	119.44	22.96	3.86	19.10
27.36	89.62	17.69	71.9	111.89	31.73	5.07	26.66
25.30	97.58	18.63	78.9	99.36	39.63	5.70	33.93
23.20	102.6	18.4	84.2	90.58	43.09	5.83	37.26
20.41	106.2	17.7	88.5	78.00	47.06	5.32	41.74
19.85	106.6	17.5	89.1	73.06	48.64	5.08	43.56
19.33	107.0	17.5	89.5	67.64	50.52	4.72	45.80
17.90	107.8	16.6	91.2	64.73	51.64	4.41	47.23
17.10	108.1	16.0	92.1	0	71.5	0	71.5
16.34	108.5	15.0	93.5				
15.86	108.7	14.8	94.9				
14.82	109.3	13.7	95.6				
0	112.	0	112.				

After having calculated the  $L_0$  and  $\sigma_0$  from the extrapolation values thus obtained, we get the following survey, (To give some idea of the order of magnitude the kinetic energy per degree of freedom at the critical temperature ( $kT_k$ ) and the dissociation energy<sup>1)</sup> per molecule have been added).

Let us start with the relation of  $\sigma_0$  and  $L_0$ . For nitrogen and argon this is within the margin of errors  $\frac{1}{4}$ , for oxygen 0.267. It seems, therefore, that though oxygen is hexagonal, the strength of the bonds in the

<sup>1)</sup> J. J. VAN LAAR. Die Zustandsgleichung p. 215.

Argon				Oxygen			
$T$	$L$ (gr. cal.)	$W$	$L_i$	$T$	$L$ (gr. cal.)	$W$	$L_i$
147.92	10.50	2.19	8.31	152.7	11.23	2.91	8.32
141.55	18.53	3.28	15.25	149.8	18.62	3.50	15.12
137.58	21.74	3.32	18.42	143.2	28.15	4.85	23.30
132.89	24.73	3.88	20.85	132.9	36.72	5.46	31.26
122.33	29.62	4.55	25.07	118.6	43.54	5.61	37.93
111.86	33.02	4.66	28.36	91.1	50.29	5.04	45.25
97.70	36.50	4.45	32.05	62.7	56.44	3.45	52.99
89.94	38.15	3.97	34.18	0	70.0	0	70.0
0	59.0	0	59.0				

	$L_0 \cdot 10^{14}$	$\sigma_0 \cdot 10^{14}$	$kT_k \cdot 10^{14}$	$D, E_n \cdot 10^{14}$
H <sub>2</sub>	1.55	0.62	0.456	600
N <sub>2</sub>	13.9	3.47	1.729	1000
A	16.3	4.10	2.067	
O <sub>2</sub>	15.5	4.12	2.116	1100

different directions does not differ much. In hydrogen, though it is regular, the ratio is  $\frac{\sigma_0}{L_0} = 0.40$ .

In conformity with a remark by EINSTEIN (loc. cit.) that in substances with very small molecules the radius of the molecular sphere of action would be greater than three times the radius of the molecule, and taking into consideration the poly-planed crystalline structure, we might try to account for this by assuming that every hydrogen molecule has two kinds of rods. We must then distinguish two groups of rods, the first with number  $k_1$ , length  $l_1$ , and strength  $s_1$ , the second with  $k_2$ ,  $l_2$ ,  $s_2$ .

We may make the following plausible supposition:  $l_2 = 2l_1$ , and  $k_2 = 2^2 k_1$ , because probably  $\frac{k_2}{k_1} = \frac{4\pi l_2^2}{4\pi l_1^2} = \frac{l_2^2}{l_1^2}$  will hold.

Then the formulae become:

$$K_0 = \frac{N}{2} (k_1 s_1 + k_2 s_2) \quad T_0 = \frac{N}{8} (k_1 l_1 s_1 + k_2 l_2 s_2)$$

$$K_0 = \frac{N}{2} k_1 (s_1 + 2^2 s_2) \quad T_0 = \frac{N}{8} k_1 l_1 (s_1 + 2^3 s_2)$$

$$\frac{T_0}{K_0} = \frac{l_1 s_1 + 2^3 s_2}{4 s_1 + 2^2 s_2}$$

Taking  $\frac{\sigma_0}{L_0} = 0.40$  (hydrogen), we find from the formula:

$$\frac{\sigma_0}{L_0} = \frac{1}{4} + \frac{s_2}{s_1 + 2^2 s_2} \text{ or } s_2 = 0.37 s_1.$$

When we extend this procedure to  $n$  kinds of rods, we get the following:  $l_n = n l_1$  and  $k_n = n^2 k_1$ .

$$\frac{T_0}{K_0} = \frac{l_1 s_1 + 2^3 s_2 + 3^3 s_3 + \dots + n^3 s_n}{4 s_1 + 2^2 s_2 + 3^2 s_3 + \dots + n^2 s_n}$$

and in this a definite course of  $s$  gives a definite ratio of  $\frac{T_0}{K_0}$ , hence also of  $\frac{\sigma_0}{L_0}$ . On transition of  $n$  to infinite we should then get back the integrals of the beginning.

I think it, however, necessary to point out that there is some doubt about the correctness of the data for hydrogen. SIMON and LANGE believe they have observed a maximum in the heat of evaporation<sup>1)</sup> and the formula for  $\sigma$  in hydrogen departs from the formulae of the three other gases. In the three latter gases the temperature at which  $\sigma = 0$ , is smaller than the critical, whereas it is greater in hydrogen.

As regards the order of magnitude we might expect according to the formula of EÖTVÖS, that  $kT_k$  should be of the same order. It is, however, surprising in nitrogen and argon that  $L_0$  and  $\sigma_0$  are a whole number of times  $kT_k$ .

In these simple substances the energies of dissociation are many times greater than the heats of evaporation, the ratio for water of 0° C. on the contrary being about 6 to 1.

The method of comparing  $\sigma_0$  and  $L_0$  followed here cannot be applied for less simple substances. Not only does the extrapolation become more and more doubtful in consequence of the rise of the melting-point, but besides it is necessary to know something about the position of the molecule in the surface, this being of great influence on the number of molecules per  $\text{cm}^2$ . In an imaginary plane intersecting the liquid, not the same number of molecules will be present as in a  $\text{cm}^2$  of the surface. Nor will the reasoning be valid for not regularly crystallizing substances, because the molecules will assume a definite orientation in the surface

<sup>1)</sup> Zeitsch. für Phys. Bd. 15. (1923) p. 312. The two values through which they conclude to a maximum, differ only about 10%.

<sup>2)</sup> Leiden Comm. phys. lab, Suppl. N<sup>o</sup>. 23. and Enc. der Math. Wiss. Art. V 10 note 528.

not only dependent on the form, but also on the difference of force in the different directions.

At the conclusion of this article it is a privilege to me to express my indebtedness to Prof. Dr. H. A. LORENTZ for the readiness with which he always put his time at my disposal to discuss these questions with me. To him, and to Prof. Dr. W. H. KEESOM, to whom I also express my thanks here, I owe many a valuable suggestion.

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**Mathematics.** — “The Complete System of Invariants of Two Covariant Antisymmetrical Tensors of the Second Order and an arbitrary Number of Vectors”. By G. F. C. GRISS. (Communicated by Prof. R. WEITZENBÖCK).

(Communicated at the meeting of March 28, 1925).

1. We start from a system of 2 antisymmetrical tensors  $p_{ik}$  and  $q_{ik}$  and  $r$  covariant vectors  ${}_1a_i, \dots, {}_ra_i (i, k = 1, \dots, n)$  and we shall determine its complete system of invariants by the aid of the symbolical method<sup>1)</sup>.

We write symbolically

$$p_{ik} = p_i p_k = -p_k p_i \quad (i, k = 1, \dots, n),$$

where  $p_1 \dots p_n$  are complex symbols<sup>1)</sup>, and we introduce aequivalent complex symbols

$$(p_i)_1 = (p_i)_2 = (p_i)_3 = \dots$$

The same with  $q_{ik}$ .

According to the first principal theorem of the symbolical method any whole rational invariant of the given tensors is a sum of products of bracket-factors of the following form:

$$(p_1^2 \dots p_\mu^2 p_{\mu+1} \dots p_\nu \ q_1^2 \dots q_\lambda^2 q_{\lambda+1} \dots q_\kappa \ {}_1a \dots {}_\sigma a) \quad \mu + \nu + \lambda + \kappa + \sigma = n. \quad (1)$$

For  $\mu = \nu$  and  $\lambda = \kappa$  the bracket-factor is itself an invariant and we shall prove the

**THEOREM:** *The (smallest) complete system of invariants of the antisymmetrical tensors  $p_{ik}$  and  $q_{ik}$  and the vectors  ${}_1a_i, \dots, {}_ra_i$  are formed by the following brackets*

$$(p_1^2 \dots p_\mu^2 q_1^2 \dots q_\lambda^2 \ {}_1a \dots {}_\rho a) \quad \dots \quad (2)$$

If the number of vectors is  $\cong n$ , there are of course invariants without  $p$  and  $q$ , e.g.  $({}_1a \dots {}_na)$ . If  $n$  is even there are invariants without  $a$ 's, to wit

$$(p_1^2 \dots p_\mu^2 q_1^2 \dots q_\lambda^2).$$

2. **PROOF.** We consider an invariant  $I$  consisting of a product of brackets and containing in particular (1) where  $\mu \neq \nu$  and  $\lambda \neq \kappa$ . Find the other bracket containing the symbol  $p_{\mu+1}$  and transform by the aid of an identity of the symbolical method so that this 2<sup>nd</sup> symbol gets into (1). We find:

<sup>1)</sup> Cf. R. WEITZENBÖCK. Invariantentheorie. Groningen (1923). Especially Abschnitt III.

$$\begin{aligned}
 & (2\mu+2) (p_1^2 \dots p_\mu^2 p_{\mu+1} \dots p_\nu q_1^2 \dots q_\lambda^2 q_{\lambda+1} \dots q_{\nu-1} a \dots a) (p_{\mu+1} \dots) = \\
 & = (-1)^{\nu-\mu} 2\lambda (p_1^2 \dots p_{\mu+1}^2 p_{\mu+2} \dots p_\nu q_1^2 \dots q_{\lambda-1}^2 q_\lambda q_{\lambda+1} \dots q_{\nu-1} a \dots a) (q_\lambda \dots) + \\
 & + \sum_{\pi} (-1)^{\pi} (p_1^2 \dots p_{\mu+1}^2 p_{\mu+2} \dots p_{\mu+\pi-1} p_{\mu+\pi+1} \dots p_\nu q_1^2 \dots q_\lambda^2 q_{\lambda+1} \dots q_{\nu-1} a \dots a) (p_{\mu+\pi} \dots) + \\
 & + \sum_{\tau} (-1)^{\nu-\mu+\tau} (p_1^2 \dots p_{\mu+1}^2 p_{\mu+2} \dots p_\nu q_1^2 \dots q_\lambda^2 q_{\lambda+1} \dots q_{\lambda+\tau-1} q_{\lambda+\tau+1} \dots q_{\nu-1} a \dots a) (q_{\lambda+\tau} \dots) + \\
 & + \sum_{\rho} (-1)^{\nu-\mu+\rho-\lambda+\tau} (p_1^2 \dots p_{\mu+1}^2 p_{\mu+2} \dots p_\nu q_1^2 \dots q_\lambda^2 q_{\lambda+1} \dots q_{\nu-1} a \dots a_{\rho-1} a_{\rho+1} \dots a) (\rho a \dots)
 \end{aligned} \tag{3}$$

We have written  $I$  as a sum of invariants where (1) is replaced by a bracket-factor which contains the square of one more symbol  $p$ . By continuing this we split  $I$  into invariants each of which contains a bracket-factor in which all the symbols  $p$  are quadratic. Finally we can obtain that the symbols  $p$  are quadratic in all the brackets. In this case all the brackets have the form:

$$(p_1^2 \dots p_\mu^2 q_1^2 \dots q_\lambda^2 q_{\lambda+1} \dots q_{\nu-1} a \dots a) \dots \tag{4}$$

We apply a similar transformation as (3):

$$\begin{aligned}
 & (2\lambda+2) (p_1^2 \dots p_\mu^2 q_1^2 \dots q_\lambda^2 q_{\lambda+1} \dots q_{\nu-1} a \dots a) (q_{\lambda+1} p^2 \dots q_\nu \dots a) = \\
 & = -2\mu (p_1 p_2^2 \dots p_\mu^2 q_1^2 \dots q_\lambda^2 q_{\lambda+1}^2 q_{\lambda+2} \dots q_{\nu-1} a \dots a) (p_1 p^2 \dots q_\nu \dots a) +
 \end{aligned} \tag{5}$$

+ terms which contain one symbol  $q$  more quadratically and which consist again of brackets of the type (4). We transform the first term once more by conveying  $p_1$  out of the first bracket-factor into the second. In this way we split our invariant  $I'$  into invariants with brackets of the type (4) which contain either a symbol more quadratically or a bracket-factor that contains a symbol  $q$  more and a symbol  $p$  less quadratically than (4). If we continue this we get, apart from the invariants which contain a symbol more quadratically, invariants of which the 1<sup>st</sup> bracket-factor has the form

$$(q_1^2 \dots q_\lambda^2 q_{\lambda+1} \dots q_{\nu-1} a \dots a) \dots \tag{6}$$

The last of these transformations leads to exclusively invariants that contain one symbol more quadratically, and of which the brackets have kept the type (4).

If we continue this long enough we obtain a whole rational function of brackets in which all the symbols are quadratic.

The form of the invariants shows directly that the complete system of invariants (2) cannot be replaced by a smaller one.

3. We shall now treat the case that, besides  ${}_1a_i, \dots, {}_r a_i, p_{ik}$  and  $q_{ik}$  an arbitrary number of contravariant vectors  ${}_1u^i, \dots, {}_s u^i$  are given. In this case we have, besides (1), symbolical factors of the following types:

$$(i_1 u' \dots i_n u'), \dots \dots \dots (7)$$

$$(i_a h u'), \dots \dots \dots (8)$$

$$(p h u') \dots \dots \dots (9)$$

and

$$(q h u'), \dots \dots \dots (10)$$

where  $i_1, \dots, i_n$  are  $n$  numbers out of  $1, \dots, s$  and  $l=1, \dots, r, h=1, \dots, s$ .

(7) and (8) are invariants; with (9) and (10) we form directly the invariants

$$(p h u') (p l u') \dots \dots \dots (11)$$

and

$$(q h u') (q k u') \dots \dots \dots (12)$$

where

$$h, k = 1, \dots, s, \quad h \neq k.$$

If now we choose again an invariant which is a product of symbolical factors, we may at once disregard factors of the types (7) and (8) and we need only consider the types (1), (9) and (10). Now the factors of type (1) can contain a symbol  $p$  of which the aequivalent symbol is contained in  $(p h u')$ . Disregarding such symbols  $p$  and  $q$ , which we shall indicate resp. by  $\pi$  and  $\varrho$ , we can, according to the proof given above, reduce all the brackets of the type (1) to the more simple type

$$(p_1^2 \dots p_\mu^2 q_1^2 \dots q_\nu^2 \pi_1 \dots \pi_\lambda \varrho_1 \dots \varrho_\lambda a \dots \sigma a) \dots \dots (13)$$

In this case, however, the invariant that contains this factor, may be split into the product of 2 invariants of which one has the type

$$\left. \begin{aligned} &(p_1^2 \dots p_\mu^2 q_1^2 \dots q_\nu^2 \pi_1 \dots \pi_\lambda \varrho_1 \dots \varrho_\lambda a \dots \sigma a) (\pi_{1 \lambda} u') \dots \\ &\dots (\pi_{\lambda \lambda} u') (\varrho_{1 \lambda+1} u') \dots (\varrho_{\lambda \lambda+2} u'). \end{aligned} \right\} (14)$$

We can continue in an analogous way with the other factor. There remains, therefore, only the invariant (14) to investigate. We transform all the  $\varrho_\lambda$  in the 1<sup>st</sup> factor. This fails only when at a given moment that first factor does not contain any  $\pi$  or  $p$ ; in this case we have

$$(q_1^2 \dots q_\nu^2 \varrho_1 \dots \varrho_\lambda a \dots \sigma a) (\varrho_{1 \lambda} u') \dots (\varrho_{\lambda \lambda} u') \dots \dots (15)$$

multiplied by invariants of the type (11), (15), however, gives invariants of the types (2) and (12).

Consequently there remains:

$$(p_1^2 \dots p_\mu^2 q_1^2 \dots q_\nu^2 \pi_1 \dots \pi_\lambda a \dots \sigma a) (\pi_{1 \lambda} u') \dots (\pi_{\lambda \lambda} u') \dots (16)$$

We remark that  $\lambda \equiv n$  and we may disregard those invariants (16) for which  $2\nu \equiv \lambda$ ; in this case we transform all the  $q$ 's out of the former factor into the latter.

**THEOREM:** *The smallest complete system of invariants of the antisymmetrical tensors  $p_{ik}$  and  $q_{ik}$  and an arbitrary number of covariant and contravariant vectors is*

$$\begin{aligned} & (i_a \mu'), \quad (i_i u' \dots i_n u'), \quad (p_{h u'})(p_{k u'}), \quad (q_{h u'})(q_{k u'}), \\ & (p_1^2 \dots p_\mu^2 q_1^2 \dots q_\lambda^2 a \dots a), \\ & (p_1^2 \dots p_\mu^2 q_1^2 \dots q_\nu^2 \pi_1 \dots \pi_\lambda a \dots a) (\pi_{i_1} u') \dots (\pi_{i_\lambda} u') \quad (2\nu > \lambda > 0; i_\alpha \neq i_\beta). \end{aligned}$$

It remains still to show that this system is the smallest. For this we need only prove that an invariant of the latter type cannot be reduced to the other invariants by the aid of the symbolical identities. We can only transform one or another  $\pi$  in the 1<sup>st</sup> factor, through which, disregarding invariants with one square more, there arises an invariant with a factor  $(\rho u')$ . We can only continue this with another  $\pi$  until all the symbols  $\pi$  are conveyed to the 1<sup>st</sup> factor. There remains, however, an invariant which does not belong to the indicated system, because, according to  $2\nu > \lambda$ , the first factor contains at least one symbol  $q$ .

4. We shall discuss a few special cases.

1. **THEOREM:** *The (smallest) complete system of invariants of an antisymmetrical tensor  $p_{ik}$  and an arbitrary number of vectors is*

$$\begin{aligned} & (i_a \mu') \quad (i_i u' \dots i_n u') \quad (p_{h u'})(p_{k u'}) \\ & (p_1^2 \dots p_\mu^2 a \dots a). \end{aligned}$$

2. *If 2 covariant vectors  $a_i$  and  $b_i$  and no contravariant ones are given, we have for  $n=2k$  the complete system*

$$\left. \begin{aligned} & (p_1^2 \dots p_i^2 q_1^2 \dots q_{k-i}^2) \quad (i=0, \dots, k) \\ & (ab p_1^2 \dots p_i^2 q_1^2 \dots q_{k-i}^2) \quad (i=0, \dots, k-1); \end{aligned} \right\} \dots \dots (17)$$

for  $n=2k+1$

$$\left. \begin{aligned} & (ap_1^2 \dots p_i^2 q_1^2 \dots q_{k-i}^2) \quad (i=0, \dots, k) \\ & (bp_1^2 \dots p_i^2 q_1^2 \dots q_{k-i}^2) \quad (i=0, \dots, k). \end{aligned} \right\} \dots \dots (18)$$

In both cases we have  $n+1$  relative, hence  $n$  absolute invariants  $I_1, \dots, I_n$ . Accordingly all algebraic absolute invariants may be expressed in these  $n$  absolute invariants. As on the other hand, the given tensors and vectors have  $2 \times \frac{1}{2}n(n-1) + 2n = n^2 + n$  independent components, we must get at least  $n$  independent absolute invariants through elimination of the coefficients of the transformation. Hence  $I_1, \dots, I_n$  are  $n$  independent absolute invariants.

3. *If 3 covariant vectors  $a_i, b_i$  and  $x_i$  are given, we have for  $n=2k$  a complete system, which, besides of (17), consists of*

$$\left. \begin{aligned} (xap_1^2 \dots p_i^2 q_1^2 \dots q_{k-i-1}^2) \quad (i=0, \dots, k-1) \\ (xbp_1^2 \dots p_i^2 q_1^2 \dots q_{k-i-1}^2) \quad (i=0, \dots, k-1). \end{aligned} \right\} \dots \dots (19)$$

For  $n = 2k + 1$  we get besides (18)

$$\left. \begin{aligned} (xp_1^2 \dots p_i^2 q_1^2 \dots q_{k-i}^2) \quad (i=0, \dots, k) \\ (xabp_1^2 \dots p_i^2 q_1^2 \dots q_{k-i-1}^2) \quad (i=0, \dots, k-1). \end{aligned} \right\} \dots \dots (20)$$

In the same way as above we find in both cases  $2n$  independent absolute invariants. We find in particular  $n$  independent absolute invariants  $(x, {}_h a')$ , which we can also consider as covariants of the system  $a_i, b_i, p_{ik}$  and  $q_{ik}$ . Consequently the  $n$  contravariant vectors  ${}_h a'$  are linearly independent.

We can also prove the latter by direct calculation of the determinant  $D = |{}_h a^i|$  on the supposition that for  $n = 2k$

$$I = (abq_1^2 \dots q_{k-1}^2) \neq 0 \text{ and } I' = (p_1^2 \dots p_k^2) \neq 0,$$

whereas all the other invariants op (17) are zero; in this case we find

$$D = c I^k I'^{k-1}, \text{ where } c \neq 0.$$

For  $n = 2k + 1$  we calculate  $D$  in the same way by assuming

$$I = (a p_1^2 \dots p_k^2) \neq 0 \text{ en } I' = (b q_1^2 \dots q_k^2) \neq 0,$$

whereas all the other invariants of (18) are zero; in this case

$$D = c' I^k I'^k, \text{ where } c' \neq 0.$$

4. For 2 covariant vectors  $a_i$  and  $b_i$  and one contravariant vector  $u$  we find, besides (17) and (18), for  $n = 2k$  and  $n = 2k + 1$  resp.

$$\left. \begin{aligned} (a u') \quad (p u') (a p p_1^2 \dots p_i^2 q_1^2 \dots q_{k-i-1}^2) \quad (i=0, \dots, k-2) \\ (b u') \quad (p u') (b p p_1^2 \dots p_i^2 q_1^2 \dots q_{k-i-1}^2) \quad (i=0, \dots, k-2) \end{aligned} \right\} \dots \dots (21)$$

and

$$\left. \begin{aligned} (a u') \quad (p u') (p p_1^2 \dots p_i^2 q_1^2 \dots q_{k-i}^2) \quad (i=0, \dots, k-1) \\ (b u') \quad (p u') (a b p p_1^2 \dots p_i^2 q_1^2 \dots q_{k-i-1}^2) \quad (i=0, \dots, k-2) \end{aligned} \right\} \dots \dots (22)$$

We find again  $2n$  independent absolute invariants among which in particular  $n$  independent absolute invariants of the form  $({}_h \beta u')$ , which may be considered as contravariants of the system  $a_i, b_i, p_{ik}$  and  $q_{ik}$ .

Accordingly the covariant vectors  ${}_h \beta_i$ , defined in this way, are linearly independent. The minors of the determinant of these covariant vectors divided by the determinant give  $n$  linear independent contravariant vectors that depend linearly on the contravariant vectors  ${}_h a^i$  mentioned under 3.

5. Finally for  $n = 4$ <sup>1)</sup> we have the

THEOREM: *The (smallest) complete system of invariants of 2 antisymmetrical tensors  $p_{ik}$  and  $q_{ik}$  and an arbitrary number of vectors is formed by*

$$\begin{aligned} & ({}_i a \ h u') \quad ({}_i u' \ {}_i u' \ {}_i u' \ {}_i u') \quad (p_1^2 p_2^2) \quad (p^2 q^2) \quad (q_1^2 q_2^2) \\ & (p^2 \ {}_i a \ m a) \quad (q^2 \ {}_i a \ m a) \quad (p \ h u') (p \ u u') \quad (q \ h u') (q \ u u') \\ & \qquad \qquad \qquad (q^2 p \ {}_i a) (p \ h u'). \end{aligned}$$

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<sup>1)</sup> Cf. F. MERTENS. Invariante Gebilde von Nullsystemen. Wiener Berichte. Band XCVII (1888).

**Chemistry.** — "On the Repulsive Action of Mutually Equal and Mutually Differing Groups in Saturated Organic Compounds."  
By Prof. J. BÖESEKEN.

(Communicated at the meeting of February 28, 1925).

The increase of conductivity which boric acid undergoes in aqueous solutions through addition of ortho-dihydroxy-benzene derivatives, added to the separation of well-defined complex compounds of the type  $\left[ \text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{B} \begin{array}{c} \diagdown \text{O} \diagup \\ \diagup \text{O} \diagdown \end{array} \text{C}_6\text{H}_4 \right] \text{K}$ , whereas this influence and this kind of compounds is absent in meta- and para-derivatives, renders it pretty well certain that this phenomenon should be ascribed in the first place to the particularly favourable position of the two hydroxyl groups in pyrocatechol and its derivatives.

That this increase of conductivity does not appear, or at least in a much smaller degree, in the aliphatic 1,2 glycols, will then be owing to the less favourable position which the OH groups occupy as a rule. Below we give once more a survey of the two categories of compounds, from which the difference will be at once clear.

Compare Table 1 next page.

We have assumed that in the aromatic nucleus the C-atoms with the groups bound to them, are held in one plane<sup>1)</sup>, whereas in the saturated aliphatic compounds, in consequence of the revolvability of the molecule-parts round the single bonds as axes, the groups can assume a position imposed upon them by the mutually repulsive (and possibly sometimes also attractive) forces. The absence of an increase of the conductivity resp. the slight amount of it, might possibly also be attributed to the less acid character of the aliphatic compounds compared with that of the aromatic ones and the positive result in  $\alpha$ -chlorhydrine might be an indication in this direction. That this difference can, however, have only a very small influence, appears particularly from the study of the cis-cyclopentenediol, and of the mannitan. These two are saturated aliphatic compounds, which distinguish themselves from  $\alpha$ -glycols exclusively by their five-ring structure.

Through the presence of this ring the ring-forming atoms are held in one plane<sup>1)</sup>, and the groups attached to them cannot easily yield to the

<sup>1)</sup> The rigidity of the aromatic nucleus will be treated later on in connection with a corresponding slighter mobility of unsaturated compounds and of saturated ring-systems with at most five atoms.

mutually repulsive action. If therefore they lie on the same side of the ring these compounds must, if our deduction is correct, bring about a distinct increase of the conductivity of boric acid, which has, indeed, appeared very convincingly. (Table 1).

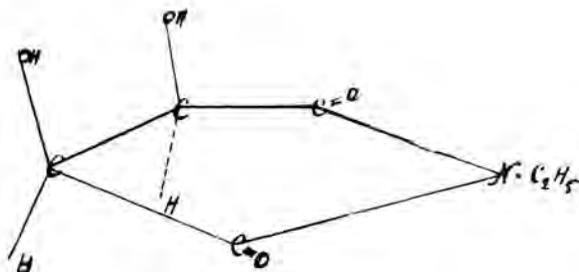
TABLE I.  
Influence of a number of polyhydroxy-compounds on the conductivity of  
0.5 mol.  $H_3BO_3$  at  $25^\circ$ .

Compound	Conc.	Increase in Kohlr.-Holb. $\times 10^6$	Compound	Conc.	Increase in Kohlr.-Holb. $\times 10^6$
Pyrocatechol	$1/32$ mol.	104	Aethylene glycol	1 mol.	—
"	0.5 "	582	"	$1/32$ "	—
Resorcinol	0.5 "	—	Propylene glycol 1.2	0.5 "	—
Hydroquinone	0.5 "	—	$\alpha$ -Chlorhydrine	0.5 "	+ 5
Phloroglucinol	$1/32$ "	—	$\alpha$ -Methylether of glycerol	0.5 "	—
Pyrogallol	0.5 "	103	$\alpha$ -Phenylether of glycerol	$1/8$ "	$\pm 0$
"	$1/32$ "	573	Pinakone	0.25 "	+ 1
Dihydroxy-naphta- line 1.2	$1/32$ "	65	Divinyl glycol	0.5 "	—
Protocatechuic acid	$1/32$ "	68			
Gallic acid	$1/32$ "	41	cis-Cyclopentandiol 1.2	0.5 mol.	about 150
Dinitropyrocate- chol 3.5	$1/256$ "	122	trans- "	1.2 "	—
4. Nitroresorcinol	$1/256$ "	—	cis-Indandiol	1.2 $1/7$ "	63
Hydroxyhydro- quinone	0.5 "	322	trans- "	1.2 " "	—
Gallic ac. methylester	$1/32$ "	212	<i>d</i> -Tartaric acid methyl-imide	0.2 "	—
Gallnut-tannin	$1/213$ "	230	Anti-tartaric-acid ethyl-imide	0.2 "	702
Dihydroxy-naphta- line 2.3	$1/200$ "	82	Mannitan	0.2 "	776

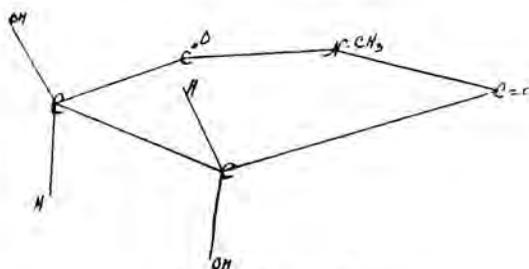
That it is entirely absent in trans-cyclopentane diol 1.2, may serve as counterproof. Remarkable is also the very different behaviour of  $\alpha$ -methyltartramide and anti-ethyltartramide (see table I and figures on next page), from which it appears that the phenomenon is qualitatively independent of the rest of the molecule, when the ring consists of only five atoms.

We shall have to devote a few words to mannitan. We have already drawn attention in earlier publications to the fact that only in the  $\alpha$ -glycols the two hydroxyl-groups, through mutual repulsion, can reach the most

unfavourable position possible for seizing the boric acid molecule, viz. on opposite sides of the axis of the C-atoms to which they are bound. Going from ethylene glycol, via glycerol, erythrol, xylitol to mannitol,



Anti-aethyltartramide.



d-Methyltartramide.

the position of two successive hydroxyl groups, even on mutual repulsion of all the hydroxyl groups, can never become so unfavourable as that in the simple  $\alpha$ -glycols.

When we imagine the chain of the C-atoms to be a straight line, the two C-OH-bonds in the glycol will form an angle of  $180^\circ$  with each other, when we take only the repulsion of the OH-groups into account; in glycerol the three corresponding bonds can form at most an angle of  $120^\circ$ , in erythrol angles of  $90^\circ$  and in mannitol angles of  $60^\circ$ .

This way of representing the problem is certainly not correct, for the axis of the C-atoms is not straight, and in the poly-alcohols with four and more OH-groups these groups will not lie along a regular screw line; it may only serve to indicate that the mutual repulsion of a number of hydroxyl groups bound to adjoining C-atoms, must force these hydroxyl groups closer together as their number increases, and must thus lead them in couples to a more and more favourable position.

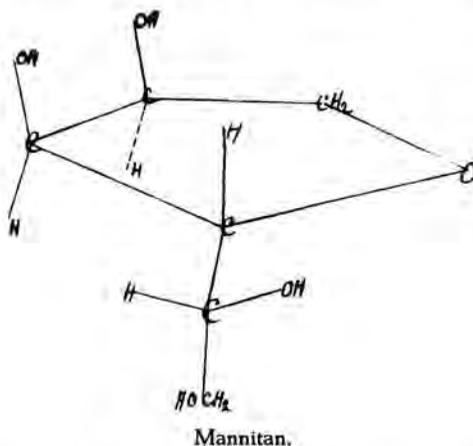
This appears to be actually the case on comparison of the action of glycol, glycerol, erythrol, and mannitol (dulcitol and sorbitol) on boric acid. (Table II). These values are the more striking when they are compared with those found for pyrocatechol (582) and pyrogallol (573), or for protocatechuic acid (68) and gallic acid (41), where a third OH-

group does not bring about an increase of the influence (Table I) and where in view of the position of these groups in space, it was not to be expected either.

TABLE II.

Compound	Conc.	Increase
Aethylene-glycol	0.5 mol.	—
Glycerol	0.5 ..	9
Erythritol	0.5 ..	64
Mannitol	0.5 ..	685
Dulcitol	0.5 ..	720
Sorbitol	0.5 ..	790
Mannitan	0.2 mol.	776
Mannitol	0.2 ..	294

When mannitan and mannitol are compared, we see that in spite of the loss of two OH-groups, the influence of the boric acid is much greater, which must undoubtedly be attributed to the fact that the two OH-groups at the C-atoms 2 and 3, have yet become more accessible to



the boric acid through their situation on the same side of the five-ring, than the *six* OH-groups in the mannitol.

We need not devote much attention to the two OH-groups of the tail, because they can repel each other as far as possible just as in a simple  $\alpha$ -glycol; we have indicated this in the symbol. Accordingly the  $\alpha$ - and the  $\beta$ -methylglucoside, where the same tail is present, and for

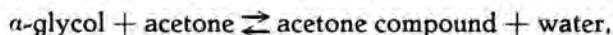
the rest also no hydroxyl groups with a favourable position, cause no increase of the conductivity of the boric acid.

While of the ethylene-glycol it is still possible to form a simple conception of the molecule in space, this becomes very difficult for the higher poly-alcohols. E. FISCHER's symbols, however excellent they may be to indicate the connection between them and the compounds to be derived from them, as sugars and hydroxylic acids, will bear but slight resemblance to the real state of equilibrium of the molecules in space. It is e.g. very well possible, and according to the measurements of the conductivity with boric acid even very probable, that the hydroxyl groups at the 2<sup>nd</sup> and 3<sup>rd</sup> or at the 4<sup>th</sup> and 5<sup>th</sup> C-atom do not lie closer to each other than any other pair of hydroxyl groups to the adjacent C-atoms. In this connection the study of the acetone compounds of mannitol is interesting. For it appeared from it that acetone combines most readily with the OH-groups at C<sub>1</sub> and C<sub>2</sub> (resp. C<sub>5</sub> and C<sub>6</sub>), from which we conclude that this is the consequence of a not unfavourable position with respect to each other and of an easy accessibility, one of them being situated at the beginning of the molecule.

Further the fact that easily *three* acetone molecules, one of which at the OH-groups of C<sub>3</sub> and C<sub>4</sub>, are absorbed, is of importance, because it appears from it that these too, though situated in the middle of the molecule, and as such certainly unfavourable, cannot lie so unfavourably with respect to each other, as FISCHER's symbol would lead us to expect.

It would, therefore, not be devoid of interest to separate the mannito-boric acid, and determine its composition and configuration.

We have here put the behaviour of mannitol towards acetone on a line with that towards boric acid. That this is allowed in aqueous acetone has appeared from investigations on the equilibrium:



of which it may be assumed in the case of analogous compounds that this will lie the more to the right as the hydroxyl groups in these glycols lie the more favourably<sup>1)</sup>. It may appear from table III that actually the constants of equilibrium of the equilibrium considered above run pretty well parallel with the increase of the conductivity of 0,5 molar boric acid. Only monochlorhydrine is an exception, hence the chlorine atom brings about a disturbance.

At any rate it is clear that with exception of *cis*-cyclopentane diol 1,2, these glycols do not easily form a compound either with boric acid nor with acetone, so that we are really justified in assuming that this is to

<sup>1)</sup> It is not allowed to apply this hypothesis indifferently to all polyhydroxy-compounds, because by the side of steric influences, also other influences will make themselves felt, especially when the nature of the molecules is very different. Compare: *Onderzoek naar de ruimtelijke konfiguratie van enkele glykolen*" by P. H. HERMANS, Proefschrift 1924.

be ascribed in the first place to the less favourable position of the two hydroxyl groups with regard to each other.

TABLE III.

Glycol	$K_{180}$	Increase of conductivity
Aethylene glycol	0.14	— 1
$\alpha$ -Monochlorhydrine	0.28	+ 7.6
Propane 1.2 diol	0.44	— 0.7
Propane 1.3 diol	0.026	— 4.0
Glycerol	0.74	+ 11.9
cis-Cyclopentanediol	10.	+149.
cis-Cyclohexanediol	0.16	— 6.2
trans- ..	0.00	— 8.4

And that they lie comparatively unfavourable is hardly to be explained in another way than by mutual repulsion, to which they can yield through the free rotation round the single bonds as axes, a repulsion which in the cases so far discussed is little opposed, if at all, by the other groups.

§ 2. With this repulsion of equal groups we have arrived at a hypothesis, which is accepted pretty generally, and which is supported by a number of observations. It is known of the carboxyl groups that they try to recede from each other as far as possible. Fumaric acid is stabler than maleic acid, and in the cyclic di-carbonic acids the cis-acid is for the greater part converted into the trans-acid on heating with acids.

This repulsion is also known of phenyl groups, as isostilbene (cis) can very easily been transformed to stilbene (trans).

As regards the glycols which are of interest here, only a few observations have been made, which confirm the mutual repulsion. In the preparation of *benzylantitartramide* by heating benzylamine-antitartrate, it was found by J. COOPS<sup>1)</sup> that anti-amide with its hydroxyl-groups in the cis-position only produced a good yield below 115°; heating at 165° gave rise to the formation of much racemate (hydroxyl groups in transposition). The same observation was made for ethyl-antitartramide: it was not even possible to prepare methyl-anti-tartramide; when methylamine-anti-bitartrate was heated at 140°—145°, necessary to effect the ring-closure, exclusively the racemate resulted.

<sup>1)</sup> Proefschrift, Delft „De Stereoisomerie der wijnsteenzuren“ pag. 60.

It was found by P. HERMANS<sup>1)</sup> that cis-hydrindene diol 1.2 and the two cis-tetrahydronaphthalene diols 1.2 and 2.3 likewise passed into their trans-isomers, when boiled with greatly diluted acids. This transformation appeared to be mutual.

As the position of the equilibrium was not the purpose of HERMANS' research, and as the knowledge of it is required to form an opinion of the mutual stability, but as the determination of this equilibrium is disturbed by the transition, with splitting off of water, into cyclic ketones, it was examined whether the *heats of combustion* of cis-trans-isomer-compounds might possibly give some information on the mutual stability.

The following table gives a survey of reliable values from the literature, from which appears how insufficient these data are. The only reliable values point to a greater heat of combustion in the cis-isomers, which was also to be expected in view of these cases.

TABLE IV.  
Heat of combustion of cis-trans isomer dicarboxylic acid.

Compound	Mol. Heat of Combustion in Cal. (p. constant).	$\Delta$
Fumaric acid <sup>2)</sup>	320.3	6.1
Maleic acid <sup>2)</sup>	236.4	
Fumaric acid <sup>3)</sup>	319.7	6.8
Maleic acid <sup>3)</sup>	326.5	
Mesaconic acid <sup>4)</sup>	477.4	2.5
Citraconic acid <sup>4)</sup>	479.9	

A few more very accurate observations may be added to these. In the first place J. COOPS<sup>5)</sup>, under guidance of Prof. VERKADE, has burned some of the tartrimes prepared by him, and has found for the mol. heat of combustion (p. const.):

d-Ethyl tartrime 671.1      d-Benzyl tartrime 1237.8  
Anti-      "      672.7 and Anti      "      1240.7.

Hence in both cases a positive difference for the cis- compared with the trans-isomer, for our purpose of more value than the values recorded in table IV, because it is here a question of  $\alpha$ -diols.<sup>6)</sup>

<sup>1)</sup> Berichte 57, 824 (1924).

<sup>2)</sup> STOHMANN, KLEBER and LANGBEIN. Journ. pr. Ch. [2] 40 202 (1889).

<sup>3)</sup> LANDOLT-BÖRNSTEIN-ROTH, Tabellen 1923 Tabel 331. Dissertatie WALLASCH.

<sup>4)</sup> STOHMANN, Zeitschr. f. physik. Ch. 10. 412 (1892).

<sup>5)</sup> Proefschrift, Delft 1924 p. 141 and 148.

<sup>6)</sup> A positive difference never can give a *proof* of a lesser stability for there are cases known the stable isomer being formed with a negative heat-effect.

At my request Mr. and Mrs. VERKADE have determined the heats of combustion of cis- and trans-hydrindene diol 1,2 and of the two 1,2,3,4 tetrahydroxynaphthalene 1,2 diols:

		$\Delta$
cis-Hydrindene diol 1.2	1098.5	1.8
trans-            "	1096.7	
cis-1.2.3.4 Tetrahydronaphthalene 1.2 diol	1251.0	1.6
trans-            "            "            "	1249.4	

With the greatest pleasure I avail myself of this opportunity to express my cordial thanks to the two investigators for their assistance. Here too the heat of combustion of the cis-modification is greater than of its trans-isomer.

It should, however, be borne in mind that these heats of combustion refer to the *solid* substances, and that we do not know the heats of melting. The melting-points of the trans-derivatives lie higher than the cis, hence the heats of melting are probably greater. To obtain perfectly comparable values, these would have to be added to the heats of combustion, which renders the difference cis-trans somewhat smaller. A reversal of the sign is, however, not to be expected, as, though the amount of the heat of melting is of the same order of magnitude (of benzene it is e. g. = 2,4 Cal.) we have to do with a difference of two heats of melting, which will certainly not differ much.

### § 3. Influence of Other Groups on Each Other, and on the Hydroxyl Groups.

It will be clear from the above that when the molecules at a chain or at a ring of five atoms bear only hydroxyl groups and hydrogen atoms, the mutual repulsion of the hydroxyl groups controls the state of equilibrium of the molecule.

This is changed when there are other groups in the molecule; even comparatively light groups, like methyl groups, will behave differently from hydrogen atoms.

This may e. g. appear from the heats of combustion of the two anhydrides of the symmetric dimethyl succinic acids determined by Mr. HARTMAN under guidance of Prof. VERKADE <sup>1)</sup>:

$$\begin{array}{l} \text{i-dimethyl succinic acid anhydride (cis) } 681.0 \\ \text{r- " " " " (trans) } 679.2 \end{array} \left. \vphantom{\begin{array}{l} \text{i-dimethyl succinic acid anhydride (cis) } 681.0 \\ \text{r- " " " " (trans) } 679.2 \end{array}} \right\} \Delta = 1.8$$

<sup>1)</sup> Not published observation.

We see that the difference in the heat of combustion is of the same order of magnitude as that of the two hydrindene diols. (See Note 6, p. 377).

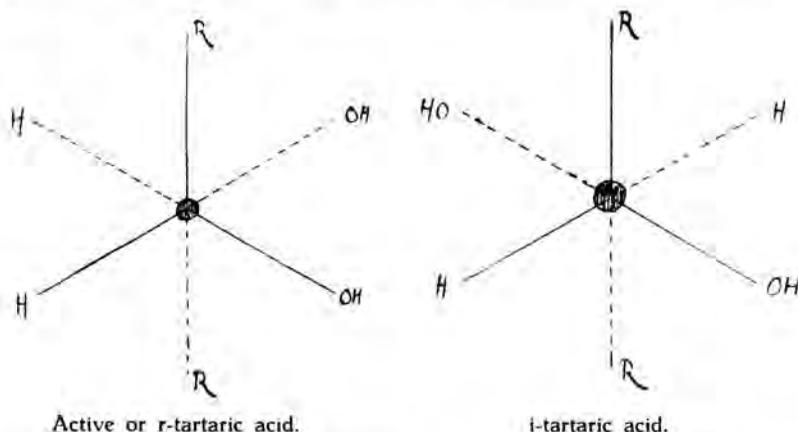
Without attaching too much value to this agreement, it is self-evident that the mutual repulsion will be of more importance between heavier groups, and especially between groups richer in electrons than between the hydroxyl groups.

The investigations by J. COOPS <sup>1)</sup> on the tartaric acids and their derivatives and those of P. HERMANS <sup>2)</sup> on the hydrobenzoin have proved this convincingly.

*Mutual repulsion of the carboxyl groups.*

In the *tartaric acids* a very great increase of the conductivity of boric acid was found in their character of  $\alpha$ -hydroxy acids, the amount of which for the rest agrees with what was to be expected from a mono-substituted two-basic di-hydroxy acid <sup>3)</sup>.

If it is, however, assumed that the mutual repulsion of the carboxyl groups considerably exceeds that of the other actions, the accumulation



of carboxyl groups and hydroxyl groups in the active acids must be greater than in the inactive acid, as is shown in the above projections, in which the plane of projection is normal to the axis of the two central C-atoms.

In consequence of this one-sided accumulation the chance to the formation of a boric acid compound in the active acids is increased, also because the hydroxyl groups are pressed closer together.

The measurements have confirmed this view, as may be derived from the subjoined table V of the observations.

We pointed out before that this configuration explains at the same time why racemic acid and its components are stronger acids than anti-

<sup>1)</sup> Proefschrif (loc. cit.) Delft.

<sup>2)</sup> Zeitschr. f. phys. Ch. **113**, 337—384 (1924).

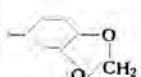
<sup>3)</sup> Recueil **40** p. 579 (1921).



Let us compare these values with those of the hydrindene diols 1.2.  $K_{18}$  for cis-hydrindene diol = 10.74 (for trans = 0.0 . . .) which glycols are to a certain extent comparable with the hydrobenzoin, then the hydroxyl groups in the r-hydrobenzoin must be situated very favourably with regard to each other.

This points to a repulsion between phenyl- and hydroxylgroups, which in the r-hydrobenzoin drives the hydroxyl groups still closer together, this action being neutralised by mutual compensation in the i-hydrobenzoin (see figures p. 379, in which R = phenyl). We will presently discuss a further proof of this repulsive action. Of the repulsion between the phenyl groups inter se indications had already been found by another

TABLE VI<sup>1)</sup>.

Name	Group R	Heat of Combustion per Mol. (p. constant)	$\Delta$
Cinnamic acid	C <sub>6</sub> H <sub>5</sub>	1041.4	6.7
Allo cinnamic acid (58°)		1048.1	
p. Oxy cinnamic acid	C <sub>6</sub> H <sub>4</sub> OH (p)	992.4	5.1
Allo p. oxy cinnamic acid		997.5	
p. Methoxy cinnamic acid	C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> (p)	1164.2	9.4
Allo p. methoxy cinnamic acid		1173.6	
Methyl cumaric acid	C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> (o)	1162.4	6.2
Methyl cumarinic acid		1168.6	
Ethyl cumaric acid	C <sub>6</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub> (o)	1317.9	6.5
Ethyl cumarinic acid		1324.4	
Propyl cumaric acid	C <sub>6</sub> H <sub>4</sub> OC <sub>3</sub> H <sub>7</sub> (o)	1472.0	6.0
Propyl cumarinic acid		1478.0	
Butyl cumaric acid	C <sub>6</sub> H <sub>4</sub> OC <sub>4</sub> H <sub>9</sub> (o)	1632.4	6.4
Butyl cumarinic acid		1638.8	
i Amyl cumaric acid	C <sub>6</sub> H <sub>4</sub> OC <sub>5</sub> H <sub>11</sub> (o)	1791.5	1.6
i Amyl cumarinic acid		1793.1	
Acetyl cumaric acid	C <sub>6</sub> H <sub>4</sub> OCOCH <sub>3</sub> (o)	1209.0	4.1
Acetyl cumarinic acid		1213.1	
Piperonyl acrylic acid		1068.8	9.0
Allo piperonyl acrylic acid		1077.8	

<sup>1)</sup> Observations by ROTH and STOERMER, Berichte **46**, 267 (1913) and WALLASCH, Thesis for the doctorate Greifswald 1913. Compare also AUWERS, ROTH, and EISENLOHR, Annalen **407**, 126 (1914).

way; it is known, among other things, that isostilbene (cis) very easily passes into ordinary stilbene (trans), and in the melting of truxillic acids, i. e. diphenylcyclobutan dicarbonic acids, with caustic potash transformations take place which can be accounted for in the simplest way by assuming that phenyl groups in the cis-position assume a trans-position.

The *repulsive action of the phenyl- on the carboxyl-group*, known from the transformation of allo- into ordinary cinnamic acid and their derivatives appears from the pretty considerable difference in the heats of combustion. (See Table VI p. 381).

We have also been able to show this action in the phenylglycerol acids<sup>1)</sup> by means of the boric acid method.

The high-melting acid (melting-point = 141°), obtained by oxidation of cinnamic acid methyl ester with KMnO<sub>4</sub> increases the conductivity more than the low melting acid (melting-point = 122°); there is in the former a greater accumulation of the OH-groups than in the latter, which should be the case when it is assumed that the phenyl- and the carboxyl-group repel each other more strongly than the two hydroxylgroups each other.

*Repulsive action of phenyl- on hydroxyl group.*

We mentioned just now a repulsive action between phenyl- and hydroxyl group, we have been accidentally able to show it in phenyl-1, cyclohexane diol 1.2.

In the preparation of this diol from the oxide through the action of diluted acid, the remarkable fact presented itself that chiefly the cis-diol was formed, whereas in all the other cases examined by us exclusively or chiefly trans-diol is formed<sup>2)</sup>, which in itself is a very remarkable case of steric reversion.

On a closer examination it appeared to me that at first trans-diol is formed also here, which can very easily be changed into the cis-isomer even in the presence of very diluted acids.

It follows from this that the cis-diol is stabler than the trans-diol, which was, besides, corroborated by a every accurate combustion<sup>3)</sup>.

The explanation lies in the repulsive action of the phenyl group at

	Heat of combustion	Δ
Phenyl 1 cis-cyclohexane diol 1.2	8132	4
.. 1 trans- .. 1.2	8136	

<sup>1)</sup> Recueil **51**, 199—207 (1922).

<sup>2)</sup> Proefschrift CHR. VAN LOON, Delft 1919 pag. 73 en 78, Recueil **40**, 519—524, 530; **41**, 205, 333, 339.

<sup>3)</sup> This too was performed under the guidance of Prof. VERKADE by Mr. MAAN. (Compare however Note 6, page 377).

C-atom 1 on the hydroxyl group at C-atom 2, which is greater than between the hydroxyl groups at 1 and 2 inter se.

*Action of the CONH<sub>2</sub>-groups on each other and on the OH-groups.* It remains to discuss the influence exercised by the tartramides on the conductivity of boric acid <sup>1)</sup>. The subjoined table VII gives a survey of the measurements:

TABLE VII.

Compound	Conc.	Increase of the conductivity of 0.5 m. H <sub>3</sub> BO <sub>3</sub> in Kohlr. Holb. $\times 10^6$
<i>d.</i> -Tartramide	0.2 m.	+ 108.0
Anti-tartramide	"	35.7
<i>d.</i> -Ethyl tartramide	"	91.6
Anti-diethyl tartramide	"	52.3
Malonic acid diamide	"	- 13.7

Here too it is seen that the active tartramide exerts a greater influence than the inactive so that the hydroxyl groups have again a more favourable position. Here, however, the explanation cannot solely lie in a preponderating mutual repulsion of the CONH<sub>2</sub>-groups. If this were the case, the anti-tartramide could not undergo a considerable *positive* action from the boric acid. (See figures p. 384; then R is CONH<sub>2</sub>).

This positive action cannot be owing to the CONH<sub>2</sub>-groups as such or to a combination of them with a hydroxyl group, as the malic acid amide does *not* exert a positive action. The resultant of the forces between the different groups must here have as consequence that also in the anti-tartramide the hydroxyl groups lie pretty favourably.

For an explanation we may make the following suppositions:

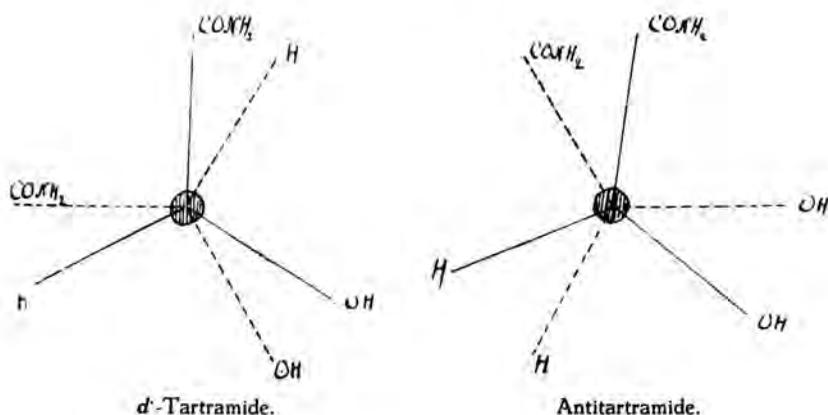
1. The repulsive action of the OH-groups is not preponderant; this is self-evident, because otherwise they could not have a favourable position.

2. The repulsive action of the CONH<sub>2</sub>-groups is not preponderant, because otherwise analogous phenomena would have been found as in the esters, i.e. no positive influence in the anti amide (see below).

3. When for the present we disregard attractive actions, it may be supposed that the CONH<sub>2</sub>- and OH-groups repel each other with greater force than those groups each other, which renders the given configurations possible.

When the CONHC<sub>2</sub>H<sub>5</sub>-groups are further assumed to repel each other still less than the CONH<sub>2</sub>-groups, the OH-groups in the active amide,

<sup>1)</sup> Proefschrift J. COOPS p. 52-55 and p. 46.



would get somewhat further apart, in the inactive amide, however, somewhat closer together, which would then be in harmony with the values found by COOPS (Table VII).

In view of the complexity of the problem and the lack of the required experimental material it is safer not to enter any further into the quantitative side of the problem.

Of this we may, however, be convinced that the mean position of equilibrium of the molecules is greatly dependent on *all* the modifications which both either the molecules themselves or the circumstances under which they are observed, undergo, and that e.g. the tartramides are, entirely differently orientated in space than the tartaric acids.

It is then obvious that the *rotary power* of optically active substances cannot be a *simple* function of the groups present in the molecule. Any change, however small it may seemingly be, changes the state of equilibrium of the molecule to such a degree, that for the present nothing can be predicted about the influence of a definite group on the amount of the rotatory power. The very extensive researches which have been made of late years in this region, have proved this convincingly. When we consider how entirely differently *d*-tartramide and *d*-tartaric acid are orientated in space, we see at once that the substitution of the basic  $\text{NH}_2$ -groups for the acid  $\text{OH}$ -groups must have a great influence on the rotation in *those* molecules, because the internal forces undergo a considerable modification. When, therefore, we wish to find regularities in this region, we must first of all consider the question: "What influence can the substitution of a definite group for an H-atom have on the state of equilibrium of the molecule?", in which the investigations by the boric acid and the acetone methods described here show us the way.

That the *principle of the optical superposition*, as it is often applied, is not valid, is clear without further discussion <sup>1)</sup>: it may qualitatively have a certain value for the establishment of some regularities, quantitatively

<sup>1)</sup> Verslag Afd. Natuurk. Kon. Akad. v. Wet., 29, 562—566.

it is sure to fall short, because the introduction of a new group brings a modification in the position of the atoms already present, just as the situation of the atoms of the introduced group undergoes a change of position through the atoms already present, and every displacement must cause a change in the amount of the rotation. The result is that placed over against the accurate investigations made of late the principle has proved entirely deficient <sup>1)</sup>.

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<sup>1)</sup> PATTERSON and TAYLOR, Journ. Ch. Soc. **87**, 33 (1905); PATTERSON and KAYE *ibid.* **89**, 1884 (1908) **91**, 705 (1907); PATTERSON and D. PATTERSON *ibid.* **107**, 142 (1915).

**Chemistry.** — "*The Constitution of the  $\alpha$ -Eleostearinic Acid from Chinese Wood Oil and from its Isomer, the  $\beta$ -Eleostearinic Acid.*" (Preliminary communication). By Prof. J. BÖESEKEN and Miss H. J. RAVENSWAAY.

(Communicated at the meeting of February 28, 1925).

The Chinese and Japanese wood-oils are obtained in China in great quantities, and used for caulking river boats, and stiffening textiles, for varnishing furniture and household things, etc.

Of late years these oils have become an important article of export, and they are put on the market in Europe in large quantities (in 1923: 80.000 tons).

They are very rapidly drying oils, polymerising on heating.

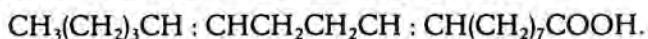
From a chemical point of view these oils occupy a particular place. Most oils are complicated mixtures of a pretty great number of glycerides; the wood-oils on the other hand consist for by far the greater part of one single glyceride of an unsaturated acid, the  $\alpha$ -eleostearinic acid, which melts at 47° and can therefore easily be obtained in pure condition by recrystallisation. Besides under different influences this acid passes into a higher melting isomer, the  $\beta$ -eleostearinic acid (melting-point 67°), which is accordingly also easily accessible.

As the glyceride of wood-oil can be converted to the higher-melting glyceride of the  $\beta$ -eleostearinic acid by illumination (melting-point = 58°), a pure unsaturated glyceride has become easily obtainable.

By reason of the analysis and the iodine-value (160—170), the constitution of a linolic acid with two double bonds  $C_{18}H_{32}O_2$  has been assigned to these eleostearinic acids, this acid having an uninterrupted chain of carbon atoms on account of its transition on reduction to stearinic acid.

As the tetrabromide of the acid, which could be obtained in very small quantities on bromination, was not identical with the tetrabromide from the linolic acid from linseed oil and poppyseed oil, it was assumed that the two double bonds occupied different places in the molecule <sup>1)</sup>.

The ozonisation has yielded the result that 50 % of the quantity of valeric acid calculated would be formed, 75 % of that quantity of azelainic acid and further a small quantity of succinic acid <sup>2)</sup>. From this the investigator concluded to the following formula:



<sup>1)</sup> B. H. NICOLET, Journ. Am. Chem. Soc. **43**, 938 (1921).

BAUER and HERBERTS, Chem. Umschau **29**, 229 (1922).

<sup>2)</sup> A. VERCRUYSE, Bull. Soc. Chim. Belg. **32**, 151—156 (1923).

Now on examination of a sample of Chinese wood-oil I was struck with the very high index of refraction. This fact is very well known, for partly the identification of this oil is based on it, but no special significance was attached to it.

When however by the aid of LORENTZ's relation:  $MR = \frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$ , we calculate the molecular refraction, and compare this value with that obtained by addition of the atomic refractions, on the supposition that the  $\alpha$ -eleostearinic acid is an unsaturate acid with two double bonds, there appears to exist a very great exaltation, even when these double bonds are assumed to be conjugated. It is 17, resp. 12.

Spec. grav. 17	Refr. 17 <sup>o</sup>	Mol. weight	Molecular Refraction		Calculated with 6 conjug. $f$
			Found	Calculat. + 6 $f$	
0.942	1.5220	878	284.6	267.6	$\pm 273$

The wood-oil itself being no pure glyceride, the  $\beta$ -glyceride was made by intensive illumination of the oil with the mercury lamp and purified by recrystallisation. Further were prepared the  $\alpha$ - and the  $\beta$ -eleostearinic acid, and the ethylester of the  $\alpha$ -eleostearinic acid.

The constants of these compounds and of the molecular refractions calculated from them, always on the supposition that they are acids or derivatives of acids with two double bonds, are the following:

Substance	Melt. point	Sp.Gr.	Refraction	Temp.	Molecular Refraction			Exaltation with regard to 2 $f$
					Calcul. for 2 $f$	Calcul. for 3 $f$	Found	
$\beta$ -glycerine-ester . . .	58 <sup>o</sup> .5	0.8991	1.5051	80 <sup>o</sup>	267.57	266.17	289.9	22.3
$\alpha$ eleostearinic acid		0.8968	1.5038	15 <sup>o</sup>	95.28	94.81	101.71	6.41
aethyl-ester	—	0.9074	1.5038	"	"	"	99.91	4.61
$\alpha$ eleostearinic acid..	47 <sup>o</sup>	0.8980	1.5080	56 <sup>o</sup>	86.04	85.57	93.05	7.0
$\beta$ -eleostearinic acid..	67 <sup>o</sup>	0.8839	1.4970	80 <sup>o</sup>	86.04	85.57	92.80	6.8
linolic acid (from poppyseed oil	—	0.905	1.4710	15 <sup>o</sup>	86.04	—	86.57	0.5

From this it appears convincingly that the exaltations are very great, they amount to between *five* and *seven* units for the *D*-line per unsaturated acid residue.

These amounts are exclusively met with in compounds with a succession of three conjugated bonds, as may appear from the following table:

Substance	Sp.Gr.	Refraction	Temp.	Molecular Refraction		Exaltation
				Found	Calculated	
Hexatriene <sup>1)</sup> . . . . .	0.7369	1.5135	15°	32.78	28.49	4.29
Allo-ocimene <sup>2)</sup> . . . . .	0.8132	1.5330	18°	52.83	46.97	5.86
Octatriene <sup>2)</sup> . . . . .	0.7938	1.5456	10° <sup>8</sup>	42.49	37.74	4.75
Methyl 5-octatriene 1.3.5 <sup>2)</sup>	0.8024	1.5335	18°	47.47	42.36	5.11

We accordingly arrive at the conclusion that a similar system of three double bonds is present in the eleostearinic acids.

To prove this both the wood-oil itself and the compounds prepared from it was hydrogenated by the aid of nickel powder; the following result was obtained:

Substance	Quantity in gr.	Absorbed H <sub>2</sub>		Calculated H <sub>2</sub>		Iodine value of hydrated substance	Temp. H <sub>2</sub>
		c.c.	Mol.	c.c.	Mol.		
Wood oil . . . . .	18.9	4050	7.9	4634	9	1.7	20°
" " . . . . .	18.5	3880	7.0	4481	9	3.1	15°
.....							
<i>α</i> -eleostearinic acid ether	16.7	3030	2.36	3863	3	2.9	20°
" "	12.2	2630	2.79	2831	3	1.2	20°
" "	12.5	2550	2.65	2894	3	1.1	18°
" "	10.3	2150	2.82	2293	3	7.3	17°

In *all* cases actually much more hydrogen is absorbed than is calculated for two double bonds. It is true that not quite three molecules of hydrogen were absorbed per molecule of fatty acid [which in the wood-oil itself may be ascribed to the presence of less unsaturated components (among others oleic acid)], but these negative differences were on an average only 0,35 mol. in the recrystallised fatty acids and in the *α*-ethylester distilled in the cathode vacuum.

<sup>1)</sup> P. MULLER, Proefschrift Utrecht 1913.

<sup>2)</sup> C. J. ENKLAAR, Recueil d. T. Ch. 36, 215 (1917). Cf. also BÖESEKEN Koolwaterstoffen II pp. 58—66.

Though we cannot yet account for the cause of this shortage, we consider the presence of a conjugated system of three double bonds in the *pure* eleostearinic acids and their esters as proved.

In the first place this constitution explains the remarkably high refraction, further the exceedingly rapid drying, and the likewise very rapid polymerisation, both of the oil and of the free fatty acids.

Besides, on account of the formation of great quantities of azelainic acid on oxidation, only the composition:



is possible, which is in perfect agreement with the presence of valeric acid<sup>1)</sup> as second important oxidation product in the action of ozon (*loc. cit.*). Only the formation of succinic acid, even though it be in small quantities, is less clear. For this reason a renewed investigation in this direction has been undertaken by us.

Finally the iodine-value seems in conflict with this conception; this is, however, only seemingly so, the investigations of the hexatrienes towards halogen having shown that they behave abnormally in this respect. (*Dissertatie MULLER*).

The details of this investigation and the further results will be published elsewhere.

*Delft*, February 1925.

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<sup>1)</sup> It may be pointed out here that MAQUENNE (*Comptes Rendus* **135**, 696 [1902]) had already shown that besides azelainic acid, valeric acid was formed in the oxidation of eleostearinic acid. By reason of his analysis he declared himself in favour of  $\text{C}_{18}\text{H}_{30}\text{O}_2$ ; hence he considered it as an isomer of the linolenic acid, without, however, having proved this. To him the honour is due of having shown that  $\beta$ -eleostearinic acid is an isomer, and no polymer of the  $\alpha$ -acid.

**Mathematics.** — “*Ueber projektive Differentialinvarianten*”. V. Von Prof. R. WEITZENBÖCK.

(Communicated at the meeting of March 28, 1925).

Wir werden hier zeigen, dass die fünf letzten Tensoren der vorigen Mitteilung auf drei ( $m = 2$ ), bzw. auf zwei ( $m > 2$ ) projektive Tensoren reduzierbar sind<sup>1)</sup>.

§ 1.

Wenn wir das Produkt  $(Yy_1 \dots y_m Z_i) \cdot y$  umformen, erhalten wir nach (66), IV (Gleichung (66) der vierten Mitteilung), d.h. also wegen

$$(v'Z_i) = (yy_1 \dots y_m Z_i) = 0$$

die Beziehung:

$$(Yy_1 \dots y_m Z_i) y = \sum_y (Yy_1 \dots y \dots y_m Z_i) y_y - (v'Y) Z_i.$$

Nun ist

$$(v'Y) = m \sqrt[m+2]{A},$$

also wird nach (70), (71) and (72), IV<sup>2)</sup>:

$$mZ_i = -y \left( \sigma_i + \varepsilon_i^h \frac{N_h}{N} \right) + \varepsilon_i^h y_h \dots \dots \dots (1)$$

Jetzt gehen wir aus von (59), IV:

$$mM y_{i(k)} = y p_{ik} + q_{ik}^{\bar{c}} y_c + g_{ik} Z \dots \dots \dots (2)$$

wo

$$\left. \begin{aligned} p_{ik} &= f_{ik} + mM_{i(k)} - mg_{ik} \frac{M^{\bar{c}} M_{\bar{c}}}{M} - mh_{ikl} M^l \\ q_{ik}^{\bar{c}} &= mMh_{ik}^{\bar{c}} + g_{ik} M^{\bar{c}}. \end{aligned} \right\} \dots \dots (3)$$

und bilden die Integrabilitätsbedingungen von (2) indem wir (2) nach  $t_l$  kovariant ableiten, dann  $k$  mit  $l$  vertauschen und subtrahieren.

<sup>1)</sup> Dass bei  $m > 2$  die dritte (quadratische) Fundamentalform im allgemeinen überflüssig wird, hat auch G. FUBINI bemerkt: Rend. Lincei V, 27 (1918), p. 150. Wie mir Herr BERWALD mitteilt, hat auch er 1923 unabhängig von FUBINI diese Tatsache festgestellt

<sup>2)</sup> Bei G. FUBINI, l.c., p. 148 ist gesetzt:

$$\lambda_i = - \left( \sigma_i + \varepsilon_i^h \frac{N_h}{N} \right) \text{ und } L_{ih} = \varepsilon_i^h.$$

Wegen

$$y_{i(k)(l)} - y_{l(i)(k)} = R_{i,kl}^{\rho} y_{\tau}$$

haben wir:

$$mM_l y_{i(k)} - mM_k y_{i(l)} + mMR_{i,kl}^{\tau} y_{\tau} = y [p_{ik(l)} - p_{il(k)}] + (y_l p_{ik} - y_k p_{il}) + \left. \begin{aligned} &+ y_{\rho} [q_{ik(l)}^{\rho} - q_{il(k)}^{\rho}] + (q_{ik}^{\rho} y_{\rho(l)} - q_{il}^{\rho} y_{\rho(k)}) + (g_{ik} Z_l - g_{il} Z_k). \end{aligned} \right\} \quad (4)$$

Hier können wir nun jedes  $y_{\rho(\tau)}$  vermöge (2) durch  $y, y_{\rho}$  and  $Z$  ausdrücken. Weiters lässt sich  $Z_l$  and  $Z_k$  nach (1) ausdrücken durch  $y$  und  $y_{\rho}$ . Hiedurch wird (4) eine lineare Beziehung zwischen den  $m+2$  Punkten  $y, y_1, \dots, y_m$  und  $Z$ , die wegen (vgl. (47) und (48), IV):

$$(yy_1 \dots y_m Z) = (v'Z) = mM \sqrt{A} \neq 0$$

$m+2$  einzelne Gleichungen ergibt. Davon ist eine von der Form  $0=0$ , nämlich diejenige, die man bekommt, wenn man die Koeffizienten von  $Z$  an beiden Seiten einander gleich stellt.

Der Koeffizient von  $y$  ergibt:

$$\left. \begin{aligned} \frac{M_l}{M} p_{ik} - \frac{M_k}{M} p_{il} &= [p_{ik(l)} - p_{il(k)}] + \left( \frac{p_{\rho l}}{mM} q_{ik}^{\rho} - \frac{p_{\rho k}}{mM} q_{il}^{\rho} \right) - \\ &- \frac{g_{il}}{m} \left( \sigma_l + \varepsilon_l^{\rho} \frac{N_{\rho}}{N} \right) + \frac{g_{il}}{m} \left( \sigma_k + \varepsilon_k^{\rho} \frac{N_{\rho}}{N} \right). \end{aligned} \right\} \quad (5)$$

Die Koeffizienten der  $y_{\rho}$ 's liefern:

$$\left. \begin{aligned} \frac{M_l}{M} q_{ik}^{\rho} - \frac{M_k}{M} q_{il}^{\rho} + mMR_{i,kl}^{\rho} &= (p_{ik} \delta_l^{\rho} - p_{il} \delta_k^{\rho}) + (q_{ik(l)}^{\rho} - q_{il(k)}^{\rho}) + \\ &+ \frac{1}{mM} (q_{ik}^{\rho} q_{\rho l}^{\sigma} - q_{il}^{\rho} q_{\rho k}^{\sigma}) + \left( \frac{g_{ik}}{m} \varepsilon_l^{\rho} - \frac{g_{il}}{m} \varepsilon_k^{\rho} \right). \end{aligned} \right\} \quad (6)$$

Multiplizieren wir (6) mit  $g^{ik}$ , dann haben wir wegen

$$g^{ik} \left( \frac{g_{ik}}{m} \varepsilon_l^{\rho} - \frac{g_{il}}{m} \varepsilon_k^{\rho} \right) = \varepsilon_l^{\rho} - \frac{1}{m} \delta_l^k \varepsilon_k^{\rho} = \frac{m-1}{m} \varepsilon_l^{\rho}$$

wenn wir noch  $m > 1$  voraussetzen und  $g^{ik} R_{i,kl}^{\rho} = -R_l^{\rho}$  berücksichtigen:

$$\left. \begin{aligned} \frac{m-1}{m} \varepsilon_l^{\rho} &= \frac{g^{ik}}{M} (M_l q_{ik}^{\rho} - M_k q_{il}^{\rho}) - mMR_l^{\rho} - g^{ik} p_{ik} \delta_l^{\rho} + \\ &+ g^{i\rho} p_{il} - g^{ik} (q_{ik(l)}^{\rho} - q_{il(k)}^{\rho}) - \frac{g^{ik}}{mM} (q_{ik}^{\rho} q_{\rho l}^{\sigma} - q_{il}^{\rho} q_{\rho k}^{\sigma}). \end{aligned} \right\} \quad (7)$$

Hiemit ist der Tensor  $\varepsilon_l^{\rho}$  durch  $g_{ik}, f_{ik}, h_{ikl}$  und die Invariante  $M$  ausgedrückt. Ist also  $M$  eine Invariante der drei Differentialformen  $g_{ik}, f_{ik}$  und  $h_{ikl}$ , so können wir sagen:  $\varepsilon_l^{\rho}$  ist auf diese drei Tensoren reduziert.

Setzen wir jetzt (7) in (6) ein, so entsteht ein System von Gleichungen

$$B_{i,kl}^{\rho} = 0 \dots \dots \dots (8)$$

und die  $B_{i,kl}^{\rho}$  sind hier aufgebaut aus den  $g_{ik}, f_{ik}, h_{ikl}, M$  und deren Ableitungen.

§ 2.

Wenn wir (5) mit  $g^{ik}$  multiplizieren, erhalten wir auf analoge Weise

$$\left. \begin{aligned} \frac{m-1}{m} \left( \sigma_l + \varepsilon_l^{\rho} \frac{N_{\rho}}{N} \right) = & -\frac{g^{ik}}{M} (M_l p_{ik} - M_k p_{il}) + g^{ik} (p_{ik(l)} - p_{il(k)}) + \\ & + \frac{g^{ik}}{mM} (p_{\rho l} q_{ik}^{\rho} - p_{\rho k} q_{il}^{\rho}). \end{aligned} \right\} (9)$$

Hier können wir nun von (7) Gebrauch machen und erhalten dadurch eine Beziehung, in der der Vektor  $\sigma_l$  ausgedrückt erscheint durch  $g_{ik}, f_{ik}, h_{ikl}$  und die beiden Invarianten  $M$  und  $N$ .

Setzen wir dagegen (9) in (5) ein, so erhalten wir ein System von Gleichungen

$$A_{i,kl} = 0, \dots \dots \dots (10)$$

das mit  $B_{i,kl}^{\rho} = 0$  zusammen die Integrabilitätsbedingungen von (2) darstellt.

Die explizite Gestalt von (8) und (10) in allgemeinen Koordinaten wird einigermaßen kompliziert. In Normalkoordinaten dagegen haben wir, wenn wir auch noch  $M = N = 1$  setzen, statt (3):

$$p_{ik} = f_{ik} \quad , \quad q_{ik}^{\rho} = m h_{ik}^{\rho} \dots \dots \dots (11)$$

Statt (7) kommt wegen  $g^{ik} f_{ik} = 0, g^{ik} h_{ik}^{\rho} = 0$ :

$$\begin{aligned} \frac{m-1}{m} \varepsilon_l^{\rho} &= -m R_l^{\rho} + f_l^{\rho} + m g^{ik} h_{il(k)}^{\rho} - m g^{ik} (h_{ik}^{\sigma} h_{\sigma l}^{\rho} - h_{il}^{\sigma} h_{\sigma k}^{\rho}) \\ \frac{m-1}{m} \varepsilon_l^{\rho} &= -m R_l^{\rho} + f_l^{\rho} + m h_{l(v)}^{\rho v} + m h_l^{\sigma v} h_{\sigma v}^{\rho} \dots \dots \dots (12) \end{aligned}$$

Hieraus finden wir z.B. für die Invariante

$$\varepsilon_{\rho}^{\rho} = \varepsilon :$$

$$\frac{m-1}{m} \varepsilon = -m R + m h^{ikl} h_{ikl} \quad \dots \dots \dots (13)$$

(6) wird in Normalkoordinaten:

$$\left. \begin{aligned} m R_{i,kl}^{\rho} = & (f_{ik} \delta_l^{\rho} - f_{il} \delta_k^{\rho}) + m (h_{ik(l)}^{\rho} - h_{il(k)}^{\rho}) + m (h_{ik}^{\sigma} h_{\sigma l}^{\rho} - h_{il}^{\sigma} h_{\sigma k}^{\rho}) + \\ & + \frac{1}{m} (g_k \varepsilon_l^{\rho} - g_l \varepsilon_k^{\rho}) \end{aligned} \right\} (14)$$

<sup>1)</sup> Bei affinen Differentialinvarianten und  $m = 2$  findet sich diese Beziehung in W. BLASCHKE, Differentialgeometrie II, Springer (1923), Gleichung (146) auf 157.

und setzen wir hier (12) ein, dann erhalten wir die Gleichungen  $B_{i,kl}^{\circ} = 0$  in Normalkoordinaten:

$$B_{i,kl}^{\circ} = -m(m-1)R_{i,kl}^{\circ} + (m-1)(f_{ik} \delta_l^{\circ} - f_{il} \delta_k^{\circ}) + m(m-1)(h_{ik(l)}^{\circ} - h_{il(k)}^{\circ}) + \left. \begin{aligned} &+ m(m-1)(h_{ik}^{\sigma} h_{\sigma l}^{\circ} - h_{il}^{\sigma} h_{\sigma k}^{\circ}) + g_{ik}(-mR_l^{\circ} + f_l^{\circ} + mh_{(l)}^{\sigma\nu} + mh_l^{\sigma\nu} h_{\sigma\nu}^{\circ}) - \\ &- g_{il}(-mR_k^{\circ} + f_k^{\circ} + mh_{k(\nu)}^{\sigma\nu} + mh_k^{\sigma\nu} h_{\sigma\nu}^{\circ}) = 0. \end{aligned} \right\} \quad (15)$$

Statt (9) haben wir:

$$\frac{m-1}{m} \sigma_l = -f_{(l)}^{\nu} - f_{\rho\sigma} h_l^{\rho\sigma} \quad \dots \quad (16)$$

und (5) lautet nun:

$$(f_{ik(l)} - f_{il(k)}) + (f_{\rho l} h_{ik}^{\rho} - f_{\rho k} h_{il}^{\rho}) = \frac{1}{m} (g_{ik} \sigma_l - g_{il} \sigma_k) \quad \dots \quad (16a)$$

Mit Hilfe von (16) bekommen wir hieraus die Gleichungen  $A_{i,kl} = 0$  in Normalkoordinaten:

$$A_{i,kl} = (m-1)(f_{ik(l)} - f_{il(k)}) + (m-1)(f_{\rho l} h_{ik}^{\rho} - f_{\rho k} h_{il}^{\rho}) + \left\{ \begin{aligned} &+ g_{ik}(f_{(l)}^{\nu} + f_{\rho\sigma} h_l^{\rho\sigma}) - g_{il}(f_{k(\nu)}^{\nu} + f_{\rho\sigma} h_k^{\rho\sigma}) = 0. \end{aligned} \right\} \quad \dots \quad (17)$$

Hieraus finden wir, dass

$$A_{i,kl} g^{kl} = 0 \quad , \quad A_{i,kl} g^{ik} = 0 \quad , \quad A_{i,kl} g^{il} = 0. \quad \dots \quad (18)$$

Auf dieselbe Weise ergibt sich nach (15):

$$B_{i,kl}^{\circ} g^{kl} = 0 \quad , \quad B_{i,kl}^{\circ} g^{ik} = 0 \quad , \quad B_{i,kl}^{\circ} g^{il} = 0 \quad , \quad B_{i,kl}^{\circ} = 0; \quad \dots \quad (19)$$

dagegen finden wir durch Verjüngung bezüglich des Indizes  $g$  und  $k$ :

$$B_{il} = B_{i,\rho l}^{\circ} = -m(m-1)R_{il} - (m-1)^2 f_{il} - m(m-1)h_{il(\rho)}^{\circ} + m(m-1)h_{\rho i}^{\sigma} h_{\sigma l}^{\circ} + \left. \begin{aligned} &+ (-mR_{il} + f_{il} + mh_{i(l)}^{\nu} + mh_l^{\nu\sigma} h_{i\sigma\nu}^{\circ}) - g_{il}(-mR + mh_{\rho}^{\sigma\nu} h_{\sigma\nu}^{\circ}) \\ &B_{il} = -m^2 R_{il} - m(m-2)f_{il} + mRg_{il} - m(m-2)h_{i(l)}^{\nu} + \left\{ \begin{aligned} &+ m^2 h_{i\rho}^{\sigma} h_{\rho l}^{\sigma} - mg_{il} h_{\rho\sigma\nu} h^{\rho\sigma\nu} = 0, \end{aligned} \right\} \end{aligned} \right\} \quad \dots \quad (20)$$

woraus sich für  $m > 2$  die Beziehung ergibt:

$$(m-2) f_{il} = -mR_{il} + Rg_{il} - (m-2)h_{i(l)}^{\nu} + mh_{\rho i}^{\sigma} h_{\rho l}^{\sigma} - g_{il} h_{\rho\sigma\nu} h^{\rho\sigma\nu} = 0. \quad (21)$$

Ist  $m = 2$ , dann haben wir:

$$(R - h_{\rho\sigma\nu} h^{\rho\sigma\nu}) g_{il} - 2R_{il} + 2h_{\rho i}^{\sigma} h_{\rho l}^{\sigma} = 0. \quad \dots \quad (22)$$

oder, da bei  $m = 2$

$$R_{ik,lm} = \frac{1}{2} R (g_{il} g_{km} - g_{im} g_{kl}) \quad , \quad R_{km} = \frac{1}{2} R g_{km}$$

ist <sup>1)</sup>:

$$g_{ii} h_{\rho\tau\nu} h^{\rho\sigma\nu} = 2 h_{\sigma i}^{\rho} h_{\rho i}^{\sigma} \dots \dots \dots (22a)$$

Aus (20) folgt schliesslich noch:

$$B_{ii} g^{ii} = 0. \dots \dots \dots (23)$$

§ 3.

Wir wollen die Gleichungen (20) und (21) auch noch in allgemeinen Koordinaten angeben. Dazu müssen wir (7) in (6) einsetzen und dann  $\varrho = k$  nehmen. Einfacher ist es, wenn wir zuerst in (6)  $\varrho = k$  setzen und dann die  $\varepsilon_i^{\rho}$  mit Hilfe von (7) eliminieren. Auf diese Weise ergibt sich aus (6) wegen

$$p_{ik} \delta_i^k - p_{ii} \delta_k^k = (1-m) p_{ii} :$$

$$(m-1) p_{ii} = -mMR_{ii} - \frac{1}{M} (M_i q_{i\rho}^{\rho} - M_{\rho} q_{ii}^{\rho}) + (q_{i\rho(i)}^{\rho} - q_{ii(\rho)}^{\rho}) + \\ + \frac{1}{mM} (q_{i\rho}^{\sigma} q_{\sigma i}^{\rho} - q_{ii}^{\sigma} q_{\sigma\rho}^{\rho}) + \frac{1}{m} (g_{i\rho} \varepsilon_i^{\rho} - g_{ii} \varepsilon_{\rho}^{\rho}),$$

also nach (7):

$$(m-1)^2 \cdot p_{ii} = -m(m-1) MR_{ii} - \frac{m-1}{M} (M_i q_{i\rho}^{\rho} - M_{\rho} q_{ii}^{\rho}) + \\ + (m-1)(q_{i\rho(i)}^{\rho} - q_{ii(\rho)}^{\rho}) + \frac{m-1}{mM} (q_{i\rho}^{\sigma} q_{\sigma i}^{\rho} - q_{ii}^{\sigma} q_{\sigma\rho}^{\rho}) + \\ + g_{i\rho} \left[ \frac{g^{\mu\nu}}{M} (M_i q_{\mu\nu}^{\rho} - M_{\nu} q_{\mu i}^{\rho}) - mMR_i^{\rho} - g^{\mu\nu} p_{\mu\nu} \delta_i^{\rho} + \right. \\ \left. + g^{\rho\sigma} p_{\sigma i} - g^{\mu\nu} (q_{\mu\nu(i)}^{\rho} - q_{\mu i(\nu)}^{\rho}) - \frac{g^{\mu\nu}}{mM} (q_{\mu\nu}^{\sigma} q_{\sigma i}^{\rho} - q_{\mu i}^{\sigma} q_{\sigma\nu}^{\rho}) \right] - \\ - g_{ii} \left[ \frac{g^{\mu\nu}}{M} (M_{\rho} q_{\mu\nu}^{\rho} - M_{\nu} q_{\mu\rho}^{\rho}) - mMR - mg^{\mu\nu} p_{\mu\nu} + \right. \\ \left. + g^{\rho\sigma} p_{\rho\sigma} - g^{\mu\nu} (q_{\mu\nu(\rho)}^{\rho} - q_{\mu\rho(\nu)}^{\rho}) - \frac{g^{\mu\nu}}{mM} (q_{\mu\nu}^{\sigma} q_{\sigma\rho}^{\rho} - q_{\mu\rho}^{\sigma} q_{\sigma\nu}^{\rho}) \right]. \quad (24)$$

Die Glieder mit  $p_{ik}$  auf der rechten Seite sind hier:

$$-g^{\mu\nu} p_{\mu\nu} g_{i\rho} \delta_i^{\rho} + g_{i\rho} g^{\rho\sigma} p_{\sigma i} + (m-1) g_{ii} g^{\rho\sigma} p_{\rho\sigma} = (m-2) g^{\mu\nu} p_{\mu\nu} g_{ii} + p_{ii}$$

Nach (3) und wegen  $g^{\mu\nu} f_{\mu\nu} = 0$  wird dabei

$$g^{\mu\nu} p_{\mu\nu} = mg^{\mu\nu} M_{\mu(\nu)} - m^2 \frac{M_{\rho} M^{\rho}}{M},$$

also unabhängig von  $f_{ik}$ . Auf der linken Seite von (24) steht also:

$$(m-1)^2 p_{ii} - p_{ii} = m(m-2) p_{ii}$$

<sup>1)</sup> Bei affinen Invarianten: W. BLASCHKE, l. c. Gleichung (150) auf p. 157.

Auf der rechten Seite setzen wir

$$q_{ik}^{\circ} = m M h_{ik}^{\circ} + g_{ik} M^{\circ} \quad , \quad q_{i\rho}^{\circ} = M_i$$

ein und erhalten:

$$\left. \begin{aligned} m(m-2)p_{il} &= -m^2 MR_{il} + mMRg_{il} + m(m-2)g_{il} M_{(\rho)}^{\circ} - \\ &\quad - m^2(m-2)g_{il} \frac{M_{\rho} M^{\circ}}{M} - m(m-2) M h_{i(\rho)}^{\circ} + \\ &\quad + m^2 M h_{\rho i}^{\circ} h_{\sigma l}^{\circ} - mMg_{il} h_{\rho\sigma\nu} h^{\sigma\nu}. \end{aligned} \right\} \quad (25)$$

Setzen wir hier schliesslich noch  $f_{il}$  aus (3) ein, so erhalten wir:

$$\left. \begin{aligned} (m-2)f_{ik} &= -mMR_{il} + g_{il}(MR + (m-2)M_{(\rho)}^{\circ} - Mh_{\rho\sigma\nu} h^{\sigma\nu}) - \\ &\quad - (m-2)Mh_{i(\rho)}^{\circ} + m M h_{\rho i}^{\circ} h_{\sigma l}^{\circ} + m(m-2)M_{\rho} h_{il}^{\circ} - m(m-2)M_{l(i)}. \end{aligned} \right\} \quad (26)$$

Diese Gleichung geht bei  $m=2$  über in (22), d.h. (22) und (22a) sind bei  $m=2$  auch in allgemeinen Koordinaten gültig und geben daher eine Beziehung zwischen den Tensoren  $g^{ik}$  und  $h_{ikl}$  unabhängig von den Koeffizienten der dritten Differentialform  $f_{ik}$ .

Bei  $m=2$  sind somit die Integrabilitätsbedingungen von (2):

1. Die Gleichungen  $B_{i,kl}^{\circ} = 0$ ; sie enthalten  $g_{ik}$ ,  $h_{ikl}$  und  $f_{ik}$ .
2. Die Gleichungen  $A_{i,kl} = 0$ ; sie enthalten gleichfalls  $g_{ik}$ ,  $h_{ikl}$  und  $f_{ik}$ .

Die Gleichungen (22) (ohne  $f_{ik}$ ) stellen keine neue Bedingung für die Koeffizienten  $h_{ikl}$  vor, denn sie sind Identitäten zwischen den  $g_{ik}$ ,  $h_{ikl}$  und deren Ableitungen. Es ist bei  $m=2$  nämlich immer möglich, durch eine Transformation  $\bar{y} = \lambda \cdot y$  zu erreichen, dass  $g_{11} = g_{22} = 0$  und  $g_{12} = -1$  wird. Aber dann ist  $R_{ik} = 0$ ,  $R = 0$ ,  $h_{112} = h_{122} = 0$  und (22) ist identisch erfüllt.

Ist dagegen  $m > 2$ , dann wird nach (21) oder auch nach (26)  $f_{ik}$  überflüssig und die Integrabilitätsbedingungen von (2) werden (wobei noch die  $p_{ik}$  nach (25) ausgedrückt sind):

1. Ein System von Gleichungen

$$*B_{i,kl}^{\circ} = 0,$$

das wir aus den Gleichungen  $B_{i,kl}^{\circ} = 0$  bekommen, wenn wir in  $B_{i,kl}^{\circ}$  die  $f_{ik}$  mit Hilfe von (26) ausdrücken.

2. Ein System von Gleichungen

$$*A_{i,kl} = 0,$$

auf dieselbe Art aus den Gleichungen  $A_{i,kl} = 0$  erhalten.

$*B_{i,kl}^{\circ}$  und  $*A_{i,kl}$  enthalten dann ausschliesslich  $g_{ik}$  und  $h_{ikl}$  und deren Ableitungen, vorausgesetzt, dass die Invariante  $M$  aus diesen Tensoren aufgebaut ist.

**Chemistry.** — “Equilibria in systems in which phases, separated by a semipermeable membrane.” VIII. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of April 25, 1925).

*The membrane-phase-rule and the membrane.*

In the previous communication we have seen that an osmotic equilibrium:

$$E = E_1(n_1 r_1) \mid E_2(n_2 r_2) \dots \dots \dots (1)$$

in which are present  $d$  substances, which diffuse by the membrane, has

$$(n_1 + n_2) - (r_1 + r_2) + 3 - d \dots \dots \dots (2)$$

freedoms. If we assume that both the separate systems  $E_1$  and  $E_2$  have the same pressure, then, therefore, equilibrium (1) has:

$$(n_1 + n_2) - (r_1 + r_2) + 2 - d \dots \dots \dots (3)$$

freedoms. We are able to deduce this and other properties also in the following way. Let us take f.i. the osmotic equilibrium:

$$E = L_1 \mid L_2 \dots \dots \dots (4)$$

in which  $L_1$  and  $L_2$  represent two liquids:

$$L_1 \text{ contains the components } A_1 B_1 \dots XY \dots UV \text{ and } W \dots (5)$$

$$L_2 \text{ .. .. } A_2 B_2 \dots XY \dots UV \text{ and } W \dots (6)$$

Consequently both liquids contain the common components  $XY \dots UV$  and  $W$ ; we assume that the  $d$  components  $UV$  and  $W$  are able to diffuse by the membrane, in contrary with the others viz.  $XY \dots$

Those components  $XY \dots$  behave, therefore, in both the liquids as if they are different substances; we may imagine them to be replaced in  $L_1$  by the components  $X_1 Y_1 \dots$  and in  $L_2$  by  $X_2 Y_2 \dots$ ; we then have two new liquids  $L'_1$  and  $L'_2$  in which

$$L'_1 \text{ contains the components } A_1 B_1 \dots X_1 Y_1 \dots UV \text{ and } W \dots (7)$$

and

$$L'_2 \text{ .. .. } A_2 B_2 \dots X_2 Y_2 \dots UV \text{ and } W \dots (8)$$

We now may imagine the osmotic equilibrium (4) to be substituted by the equilibrium:

$$E' = L'_1 + L'_2 \dots \dots \dots (9)$$

if we assume that only the components  $UV$  and  $W$  dissolve in both the liquid-phases. When in liquid  $L_1$  [viz. in (5)] the number of components is  $n_1$  and in liquid  $L_2$  [viz. in (6)] the number is  $n_2$ , then follows from (7) and (8) that equilibrium (9) consists of  $n_1 + n_2 - d$  components. Consequently, in accordance with the phase-rule of GIBBS, equilibrium (9) has:

$$(n_1 + n_2 - d) - 2 + 2 = n_1 + n_2 - d \text{ freedoms . . . . . (10)}$$

so that the osmotic equilibrium (4) has the same number of freedoms. This is also in accordance with the membrane-phase-rule; if we put viz. in (3) the number of phases  $r_1 + r_2 = 2$ , then (3) passes into (10).

We now make the same supposition for the components of system (1) as above for those of system (4); we then may imagine the osmotic equilibrium (1) to be replaced by the equilibrium:

$$E' = E'_1 + E'_2 \text{ . . . . . (11)}$$

which consists of  $n_1 + n_2 - d$  components. As there are  $r_1 + r_2$  phases, (11) and consequently also the osmotic equilibrium (1) has

$$(n_1 + n_2 - d) - (r_1 + r_2) + 2$$

freedoms; therefore, we re-find (3).

Till now with our considerations we have made no supposition on the character of the membrane and on its action; we shall call a similar membrane, the character and action of which is not defined more closely, a "theoretical" membrane.

However, we may assume also that the membrane consists of a phase  $M$ , which, under definite conditions, permits some substance to diffuse, and other ones not; we shall represent this membrane, consisting of one phase  $M$ , by  $|M|$  and call it a "real" membrane.

We now replace the theoretical membrane in (1) by a real membrane, so that we get the equilibrium

$$E = E_1(n_1 r_1) + |M| + E_2(n_2 r_2) \text{ . . . . . (12)}$$

We adjoin the following properties to this real membrane, consequently to the phase  $M$ :

1. It separates the two systems in such a way that the phases of  $E_1$  do not come in direct contact with those of  $E_2$ ;
2. It contains one or more substances  $MN$  etc., which do not occur in the systems  $E_1$  and  $E_2$  and which do not dissolve in those systems;
3. From the substances, which occur in the systems  $E_1$  and  $E_2$ , some are taken in by the membrane but others not; it forms with the taken substances a phase of variable composition.

We may imagine this real membrane f. i. as a solid solution or also as a thick, tuff, strongy viscous or jellied liquid or in another way. It

stands to reason that it depends on the character of the membrane and on its strange substances  $MN$  etc. which substances will be taken in or not from the systems  $E_1$  and  $E_2$ .

If we imagine for this real membrane a liquid, then theoretically this will probably be able to take in all substances from  $E_1$  and  $E_2$ ; practically, however, this need not be the case, the same f.i. a vapour does not contain practically all substances, which are present in the system, in which it participates.

We now are able to show: the real membrane  $|M|$  which takes  $d$  substances from the systems  $E_1$  and  $E_2$ , behaves like a theoretical membrane, by which these  $d$  substances may diffuse.

In order to show the above-mentioned, we firstly shall deduce the equations for equilibrium, which are valid for the osmotic equilibrium (1); for the sake of simplicity we assume that there is one diffusing substance only, viz.  $W$ .

We consider a system

$$E_A = A_1 + A_2 \dots + A_r \dots \dots \dots (13)$$

in which we give to an arbitrary phase  $A_i$  the composition:

$$A_i = x_i X + y_i Y + \dots + w_i W \dots \dots \dots (14)$$

$$i = 1, 2, \dots r$$

We call  $\zeta_i$  the thermodynamical potential of this phase  $A_i$ . When this system  $E_A$  is in equilibrium, then must be:

$$0 = \left. \begin{aligned} & \frac{\partial \zeta_1}{\partial X} dx_1 + \frac{\partial \zeta_2}{\partial X} dx_2 \dots + \frac{\partial \zeta_1}{\partial Y} dy_1 + \frac{\partial \zeta_2}{\partial Y} dy_2 \dots \\ & \dots + \frac{\partial \zeta_1}{\partial W} dw_1 + \frac{\partial \zeta_2}{\partial W} dw_2 \dots + \frac{\partial \zeta_r}{\partial W} dw_r \end{aligned} \right\} \dots \dots (15)$$

while the conditions:

$$\left. \begin{aligned} 0 &= dx_1 + dx_2 \dots + dx_r \\ 0 &= dy_1 + dy_2 \dots + dy_r \\ &\dots \dots \dots \end{aligned} \right\} \dots \dots \dots (16)$$

$$0 = dw_1 + dw_2 \dots + dw_r \dots \dots \dots (17)$$

must be satisfied.

From this we find in the known way the equations for equilibrium:

$$\frac{\partial \zeta_1}{\partial X} = \frac{\partial \zeta_2}{\partial X} = \dots = \frac{\partial \zeta_r}{\partial X} \quad \frac{\partial \zeta_1}{\partial Y} = \frac{\partial \zeta_2}{\partial Y} = \dots = \frac{\partial \zeta_r}{\partial Y} \quad \text{etc.} \dots \dots (18)$$

$$\frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \frac{\partial \zeta_3}{\partial W} = \dots = \frac{\partial \zeta_r}{\partial W} \dots \dots \dots (19)$$

If  $A_1$  is a phase of constant composition, viz.  $dx_1$  and  $dy_1$  satisfy the relations:

$$\frac{dx_1}{x_1} = \frac{dy_1}{y_1} = \dots = \frac{dw_1}{w_1} \dots \dots \dots (20)$$

then in (18) and (19) the terms with the index 1 disappear and we get a new equation:

$$\zeta_1 - x_1 \frac{\partial \zeta_k}{\partial X} - y_1 \frac{\partial \zeta_k}{\partial Y} \dots - w_1 \frac{\partial \zeta_k}{\partial W} \dots \dots \dots (21)$$

in which  $k$  represents one of the indices 2, 3, ...,  $r$ .

For a system:

$$E_B = B_1 + B_2 + \dots \dots \dots (22)$$

of course similar equations are valid as for  $E_A$ , consequently equations, which correspond with (15) – (21); for this reason we shall call the equations, valid for  $E_A$  the equations (15 A) – (21 A), and those, valid for  $B$ , the equations (15 B) – (21 B).

We now are able to deduce the equations for equilibrium, which are valid for the osmotic equilibrium:

$$E = E_A \mid E_B \dots \dots \dots (23)$$

in the following way. As now no more the thermodynamical potential of each of the separate systems  $E_A$  and  $E_B$  must be zero, but that of the complete system  $E$ , the equations (15 A) and (15 B) are no more valid each for itself, but we get:

$$o = (15 A) + (15 B) \dots \dots \dots (24)$$

the meaning of which is clear.

The changes  $dx_1 dx_2$  etc. which refer to the not-diffusing substances, satisfy the equations (16 A) and (16 B). As, however, the quantity of the diffusing substance  $W$  must not rest constant now in each of the separate systems  $E_A$  and  $E_B$  but it must in the complete equilibrium  $E$  the equations (17A) and (17B) disappear, therefore; they are substituted by the one equation:

$$o = (dw_1 + dw_2 + \dots)_A + (dw_1 + dw_2 + \dots)_B = 0 \dots (25)$$

Consequently for the osmotic equilibrium are valid the equations: (24), (25), (16 A) and (16 B).

If we deduce from this in the well-known way the equations for equilibrium, then we find:

the equations (18 A) and (18 B)

and still the equations:

$$\left( \frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \dots \right)_A = \left( \frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \dots \right)_B \dots \dots (26)$$

Those equations (26) involve not only the equations (19 A) and (19 B) but also still one new equation, viz.:

$$\left(\frac{\partial \zeta_k}{\partial W}\right)_A = \left(\frac{\partial \zeta_l}{\partial W}\right)_B \dots \dots \dots (27)$$

in which, as follows from (26), we may take the indices *k* and *l* arbitrarily. Consequently we find for the osmotic equilibrium (23):

1<sup>o</sup> the equations for equilibrium, which are valid for each of the systems *E<sub>A</sub>* and *E<sub>B</sub>* separately;

2<sup>o</sup> besides a new equation for equilibrium viz. (27); this expresses that the osmotic water-attraction of both the systems *E<sub>A</sub>* and *E<sub>B</sub>* is equal.

We now consider the osmotic equilibrium:

$$E = E_A + |M| + E_B \dots \dots \dots (28)$$

and we assume that the real membrane |*M*| has the composition:

$$mM + nN + oO + \dots + wW \dots \dots \dots (29)$$

and the thermodynamical potential  $\zeta$ . Instead of (24) we now get:

$$o = (15 A) + \frac{\partial \zeta}{\partial W} \cdot dw + (15 B) \dots \dots \dots (30)$$

This equation expresses that the thermodynamical potential of the complete system (28) must be a minimum. The variables *dm*, *dn* etc. of the strange substances *MN* etc. of the membrane do not occur in this equation.

The equations (16 A) and (16 B), which refer to the not-diffusing substances of the systems *E<sub>A</sub>* and *E<sub>B</sub>* rest unchanged; equation (25), however, passes into:

$$o = (dw_1 + dw_2 + \dots)_A + dw + (dw_1 + dw_2 + \dots)_B \dots \dots (31)$$

this expresses that the quantity of the diffusing substance *W*, which is present in the complete system (28), remains constant. Consequently for system (28) we have the equations: (30), (31), (16 A) and (16 B).

If we deduce from this in the known way the equations for equilibrium, then we find, besides the equations (18 A) and (18 B) still also:

$$\left(\frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \dots\right)_A = \frac{\partial \zeta}{\partial W} = \left(\frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \dots\right)_B \dots \dots (32)$$

Those equations (32) involve not only the equations (26) but yet also a new equation, viz.

$$\frac{\partial \zeta}{\partial W} = \left(\frac{\partial \zeta_k}{\partial W}\right)_A \text{ or } \frac{\partial \zeta}{\partial W} = \left(\frac{\partial \zeta_l}{\partial W}\right)_B \dots \dots \dots (33)$$

in which we may take arbitrarily the indices *k* and *l*. Consequently we find for the equilibrium (28)

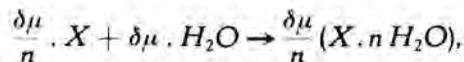
1° the same equations for equilibrium which are valid for the osmotic equilibrium (23)

2° besides a new equation (33); this expresses that the O.W.A. of the real membrane is equal to that of each of both the systems  $E_A$  and  $E_B$  separately. This equation defines also the concentration of the substance  $W$  in the membrane.

It appears from this, therefore, that the state of the separate systems  $E_A$  and  $E_B$  is defined by the same equations, immaterial whether those systems, as in (23) are in osmotic contact with the aid of a theoretical membrane, or, as in (28) with the aid of a real membrane.

Yet there may be any difference in the finishing-equilibrium of (23) and (28) if we start from definite systems (23) and (28). In the state of equilibrium of (28) viz. the real membrane must have a definite concentration of the substance  $W$ ; had this concentration beforehand been different, then the membrane must take in a little water from the systems  $E_A$  and  $E_B$  or it has to give water to them. This quantity, and consequently also the influence on the final equilibrium, can be the greater, the greater is the mass of the real membrane. If the mass of the membrane is small with respect to that of  $E_A$  and  $E_B$ , then this influence may be neglected practically.

In the previous considerations we have supposed that each of the systems  $E_A$  and  $E_B$  contains one liquid at least. This is valid, however, also, if one of the systems consists of substances of constant composition, between which a phases-reaction may occur by taking in or giving water. If one of those systems consists f. i. of a solid substance  $X$  and its hydrate  $X \cdot n H_2O$ , then on admittance of  $\delta\mu$  quantities of water occurs the reaction:



consequently a reaction, with which the quantities of the phases change, but their compositions remain constant.

We now assume that in the system  $E_A$  on increase or loss of water a similar phases-reaction may occur. The increase of the thermodynamical potential on increase of  $\delta\mu$  quantities of water, is represented by  $\frac{\partial Z_A}{\partial W} \cdot \delta\mu$  so that  $\frac{\partial Z_A}{\partial W}$  defines the O.W.A. of system  $E_A$ .

For equilibrium (23) is valid now, instead of (24):

$$o = \frac{\partial Z_A}{\partial W} \cdot \delta\mu + (15 B) \dots \dots \dots (34)$$

the equations (16 A) disappear, but (16 B) remain valid. Instead of (25) we now get, however;

$$o = \delta\mu + (dw_1 + dw_2 + \dots)_B \dots \dots \dots (35)$$

If we deduce again from this the equations for equilibrium, then we find firstly the equations (18 B) and moreover:

$$\frac{\partial Z_A}{\partial W} = \left( \frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \dots = \frac{\partial \zeta_r}{\partial W} \right)_B \dots \dots \dots (36)$$

This contains not only the equations (19B) but still one equation more; this expresses that the O. W. A. of system  $E_A$  is equal to that of system  $E_B$ .

We now take, instead of equilibrium (23) with the theoretical membrane, equilibrium (28) with the real membrane. Then we have to replace (34) and (35) by:

$$0 = \frac{\partial Z_A}{\partial W} \cdot d\mu + \frac{\partial \zeta}{\partial W} \cdot dw + (15 B)$$

$$0 = d\mu + dw + (dw_1 + dw_2 \dots).$$

We find from this again the same conditions for equilibrium (18 B) and also:

$$\frac{\partial Z_A}{\partial W} = \frac{\partial \zeta}{\partial W} = \left( \frac{\partial \zeta_1}{\partial W} = \frac{\partial \zeta_2}{\partial W} = \dots = \frac{\partial \zeta_r}{\partial W} \right)_B.$$

Those last equations contain not only the equations (36) but moreover one, which expresses that the O. W. A. of the real membrane is equal to that of the systems  $E_A$  and  $E_B$ .

Consequently it appears from this that the deduced above on the correspondance of a system with a theoretical and a real membrane, is also true, if one of the separate systems consists of substances of constant composition, between which on increase or loss of water a phasesreaction occurs.

We may extend those considerations also to an osmotic equilibrium:

$$E = E_A + |E_0| + E_B$$

in which  $|E_0|$  represents a real membrane, which consists of different phases and which has similar properties, as are discussed above for  $|M|$ . In similar way as above we find for this:

1<sup>o</sup>. the equations for equilibrium, which are valid for each of the three systems  $E_A$   $E_0$  and  $E_B$  separately;

2<sup>o</sup>. two equations, which express that the O.W.A. of the three systems is the same.

(To be continued.)

*Leiden, Lab. of Inorg. Chemistry.*

**Botany.** — “*The Radium-growth-response of one cell.*” By Prof. A. H. BLAAUW and W. VAN HEYNINGEN.

(Communicated at the meeting of February 28, 1925).

§ 1. *Introductory.*

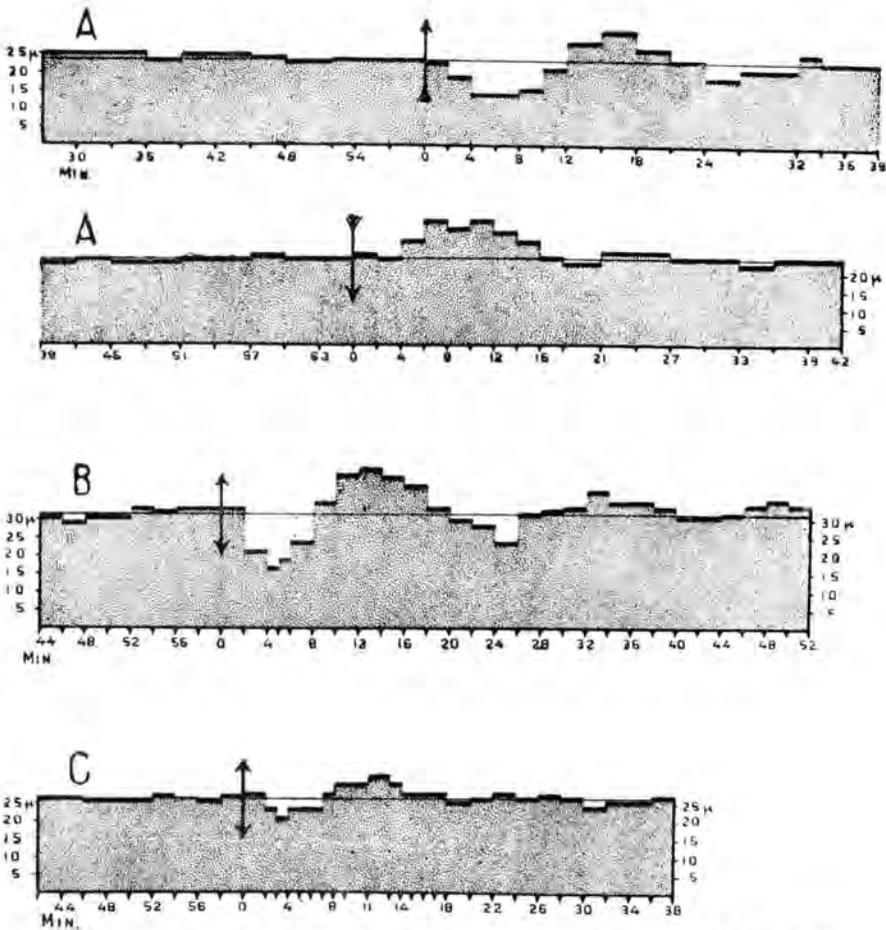
For some 10 years it has been known to us, that unicellular organs as the sporangiophores of *Phycomyces* and likewise various multicellular organs of higher plants respond to light-stimulations with characteristic accelerations and retardations of growth.

A joint discussion of the authors above-mentioned led to an investigation in the Laboratory for Plant-physiological Research at Wageningen, whether the growth of unicellular sporangiophores, so sensitive to visible light, is also affected by radium-rays.

*Method.* The experiments were made in a spacious dark room kept constantly at 17°—17.5° C., the temperature in which all previous light-investigations on *Phycomyces* were made. The cell was measured when it had reached a length of 3½—5½ cms. The mould-culture was cultivated in the same room and before the experiment it was placed for many hours in the centre of a small card-board house, partly soaked in paraffine, the wall being about 10 mms. thick. In order to observe the growth two red panes were inserted in front- and back-wall. All metal was avoided by using card-board, gum-paper and plasticine, in order to avoid secondary rays as much as possible, at least those of more penetrating power. For this purpose the culture in the card-board house and the radium-preparation (fixed on a card-board box) were placed in the middle of the room at 2 to 1½ metres distance from the stone wall and standing on high wooden tables. Radium-preparation, culture and horizontal microscope (magn. 70 ×), in which the metal could not be avoided, stood on separate tables on the concrete floor, which prevented all shaking or vibration of the tender long cells, the growth of which was to be measured.

The radium-preparation contained 9.55 mgrs. radium-element and was enclosed in a glass tube and a silver one, the latter 0.5 mm. thick. It was fixed on the cut-out rib of a small card-board box by means of a little plasticine or gum-paper. After the first experiments the silver tube (see below) was enclosed in a case of 2 mms. lead.

Whilst the growth of the mould-cell in faint red light was observed every 2 or 3 minutes through front and back-pane, the radium-preparation was placed at a certain moment at 10 or 5 cms. distance from the cell outside the



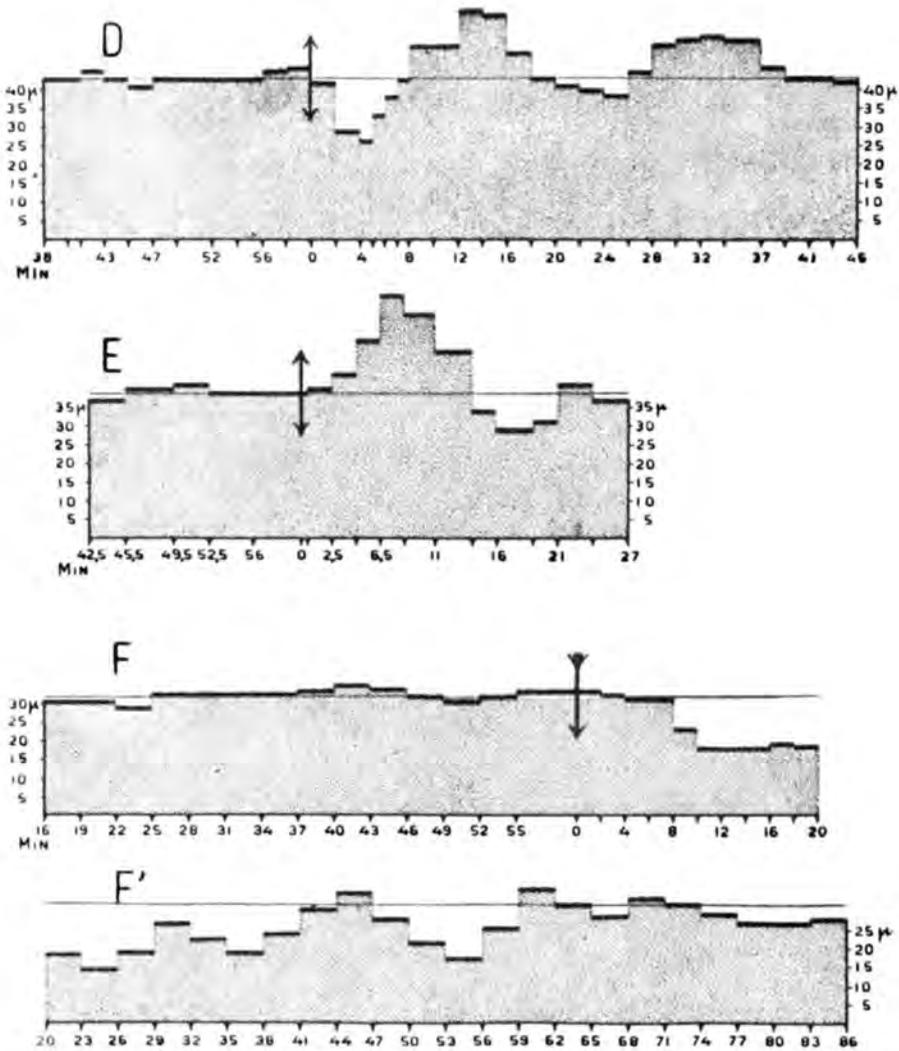
A Radium-growth-response in unintermitted exposure (66 min.) to 9,55 mgr. Radium at 10 cms distance from the cell (filters, see text). A' a continuation of A with the response to removal of radium, i.e. the radium-deradiation-response.

B Radium-growth-response after 60 seconds and C after 5 sec. exposure at 5 cms distance from the cell.

The Reactions A, B and C occurred in the dark.

house for a shorter or longer time (see below), sending its rays through one of the side-walls and placed on the same level as the growing cell.

*Tables and Figures.* The tables concerning the growth (tables 1—23) first give the growth in dark before the exposure for 20—30 minutes in 10—12 observations; the *growth of the cell in micron per minute* has been given in bold figures, i.e. the increase of length or growth averagely found during the period of time of 2—3 minutes between the points of time of observation, indicated by small figures. These periods of observation have been given in such a way that at the moment of exposure 60 is reached and we begin again at 0. Likewise at the end of an exposure of long duration the time begins at that moment at 0. Where the moment of beginning an



D Radium-growth-response of a cell, after 4-sided illumination for hours together with an intensity of 4 M.K. and exposed in that light for 60 sec. to the Ra-preparation at 5 cms distance (cf. B).

E Corresponding graphic representation of response of growth to light by M.K.S. (after one of the experiments of 1914).

F Dark-growth-response after 4-sided illumination in 4 M.K. for 5 hours, continued in F'.

exposure ( $\uparrow$ ) or ending an exposure ( $\downarrow$ ) does not coincide with an observation, the moment 0 with the arrow has been put between brackets.

The graphic representations have been construed in strict accordance with the tables. This time there has not been made a *natural* smooth curve as in previous publications, as is certainly more according to reality, but the average rate of growth during each period of time between two observations, has been indicated by a thick horizontal line. Every one can imagine the

smooth curve as he thinks it most in accordance with reality. A thin straight drawn line indicates the rate of growth (according to the preceding observations) as it would have been, if no change of surroundings had occurred. Moments of observations have been indicated by dots against the abscis. Exposures of long duration begin at ↑ and eventually at ↓; exposures lasting 60 sec. or shorter have been indicated ↓.

§ 2. *Radium-growth-response. Result of exposure and of removal of radium (de-radiation).*

To begin with we subjoin 8 tables as a result of the first experiments. The cell was exposed at 10 cms. distance from a certain point of time for a long time or permanently. It was directly evident that these cells give a striking reaction to that exposure. Influence and reaction are outwardly perceptible in a characteristic response of growth. Of course this *radium-growth-response* is a secondary phenomenon as a result of more primary responses or modifications, brought about in the metabolism of the cell by the influence of the rays, but which are for the present absolutely beyond our understanding. These more profound, primary events brought about by radiation (light, radium or other rays) may be approximated more and more in means of growth-responses. The question is, whether in future in this sphere so dark to our understanding the biologist will meet the physicist and the chemist, who ascertain the most elementary properties of rays and matter from another viewpoint and give a foundation to the whole.

The *light-growth-response* (response to rays from the visible spectrum and the ultra-violet) is characterised in these cells by an acceleration of growth (positive response of growth) beginning after at least 3 minutes and changing into a temporal retardation of growth, etc. The *radium-growth-response* is just contrary to the *light-growth-response*, so negative, i.e. beginning with a strong decrease of growth, then on account of a contra-reaction passing into an acceleration of growth, while finally, also by permanent exposure the growth recovers its equability. Judging from these experiments, the rate of growth *averagely* becomes the same as before the exposure to *this* intensity. In order to be sure whether under the influence of permanent exposure the equable growth afterwards attained deviates some percents from the rate of growth before the exposure, a great number of long experiments is required to reduce the mean error sufficiently. It may be that larger quantities of radium placed nearer, will give more striking results in this respect. To answer all these questions further investigations will be wanted.

*The radium-growth-response follows quicker than the light-growth-response; it is perceptible after an average of 2 minutes, the response to light averagely after 3½ minutes. The greatest depression after radium-exposure*

is reached after about  $5\frac{1}{2}$  minutes, the maximum of growth after light-exposure averagely after about 7 minutes (See tables 1—6) the summary in tab. 14, figure A compared to fig. E).

It should be pointed out here, that the cells of *Phycomyces* were subjected to one-sided exposure, that they never show a trace of curvatures, that on the other hand a strong growth-response follows on one-sided radium-exposure. But these rays are not refracted and they pass through these thin cells of such matter in such a way that there is no question of any practical difference of intensity within the cell. On account of this no unequal growth-response arises in the different sides of the growing zone of these cells and so no curvature is found. Refrangible light we have to supply on all sides, for if we supply on one side, the light-growth-response is found as well, but inequilateral on account of refraction of light and subsequent differences of intensity, and there soon appear the well-known phototropic curvatures.

Initially in the first experiments the glass tube containing the radium preparation was only enclosed in a silver tube,  $\frac{1}{2}$  mm. thick. Both the gamma-rays and a considerable part of the beta-rays could reach the cell through glass, silver and card-board. Soon after the silver enclosure was surrounded by 2 mms. lead to intercept the  $\beta$ -rays. To keep off the secondary  $\beta$ -rays caused in the lead-covering by the gamma-rays, a screen of 5 mms. aluminium was placed in front of it, and to intercept the fainter  $\beta$ -rays, which the gamma-rays should cause in the aluminium-layers, 10 mms. card-board were added. Even though in this way faint and soft secondary  $\beta$ -rays could not be absolutely avoided, yet at any rate by far the greater part of the  $\beta$ -rays were removed from the experiments while 80 to 90 % of the gamma-rays were preserved. The result was that the response was exactly the same, both as to nature and intensity. If a very great number of experiments were made and the intensity of response computed, taking the mean error into account, a slight decrease might be proved, the gamma-rays having also slightly lost in strength. But for the present our chief result is : *The radium-growth-response is caused by the gamma-rays, not by the beta-rays of the preparation.*

As a precaution it should be observed : 1. that the possibility exists that those gamma-rays indirectly exert this influence through  $\beta$ -rays secondarily formed outside or even inside the cell ; 2. that it is not impossible that these cells should show some sort of reaction to much stronger  $\beta$ -rays without gamma-rays.

In the further experiments the above-mentioned filter-layers 2 mms. Pb + 5 mms. Al. + 10 mms. cardboard, were always used.

After prolonged exposure the growth becomes steady fairly soon after an initially strong oscillation, so that the rate of growth observed in successive short periods varies no more than before the exposure (as a rule less than 10 %, which may be due to the method of observation or to natural slight

oscillations). When this had been the case for a long time and the radium-growth-response was outwardly finished, the radium-preparation was removed. To be quite sure the rate of growth was observed for some time after and it suddenly appeared, that some minutes after the exposure had been stopped, a growth-response followed, the reverse of the radium-growth-response, beginning a little later and attaining its maximum acceleration somewhat later: the growth soon gets normal again. This was repeated several times after long exposures of various duration (47—159 minutes): the same phenomenon was repeated, of which the tables 3—8

TABLE 1. *Permanent exposure.*

23	32	26	29	29	30 <sup>1</sup> / <sub>2</sub>	32	30 <sup>1</sup> / <sub>2</sub>	35	30 <sup>1</sup> / <sub>2</sub>	38	32	41	30 <sup>1</sup> / <sub>2</sub>	44	33 <sup>1</sup> / <sub>2</sub>
47	33 <sup>1</sup> / <sub>2</sub>	59	32	53	31	56	30 <sup>1</sup> / <sub>2</sub>	60	↑ 30 <sup>1</sup> / <sub>2</sub>	2	16	5	20	8	31
10	35	12	35	14	35	17	37	20	41 <sup>1</sup> / <sub>2</sub>	23	29	28	26 <sup>1</sup> / <sub>2</sub>		
30	31	33	24	35	29 <sup>1</sup> / <sub>2</sub>	38	37	41	32	44	33 <sup>1</sup> / <sub>2</sub>	47	29	50	32
53	29 <sup>1</sup> / <sub>2</sub>	56	32	59	33 <sup>1</sup> / <sub>2</sub>	62	33 <sup>1</sup> / <sub>2</sub>	65	32	68	32	72			

TABLE 2. *Permanent exposure.*

30	19	33	19	36	19	39	19	42	19	45	21	48	21 <sup>1</sup> / <sub>2</sub>	51	20	54	21
57	21	60	↑ 19	3	13	6	13	9	17 <sup>1</sup> / <sub>2</sub>	12	21	15	27	18	29	19	25 <sup>1</sup> / <sub>2</sub>
21	25	24	21	27	16	30	25	33	22 <sup>1</sup> / <sub>2</sub>	36	24	39	24	42	27	45	23
48	26 <sup>1</sup> / <sub>2</sub>	51	27	54	24	57	23	60									

TABLE 3. *Permanent exposure and de-radiation after 49 minutes.*

43	33 <sup>1</sup> / <sub>2</sub>	46	36	49	36	51	35	53	33 <sup>1</sup> / <sub>2</sub>	55	33 <sup>1</sup> / <sub>2</sub>	57	35		
60	↑ 31	2	24	4	20 <sup>1</sup> / <sub>2</sub>	6	27 <sup>1</sup> / <sub>2</sub>	8	33 <sup>1</sup> / <sub>2</sub>	10	43	12	45 <sup>1</sup> / <sub>2</sub>		
14	45 <sup>1</sup> / <sub>2</sub>	15	43	17	38 <sup>1</sup> / <sub>2</sub>	19	38 <sup>1</sup> / <sub>2</sub>	21	37	24	36	26	36		
28	36	30	36	32	32 <sup>1</sup> / <sub>2</sub>	35	33 <sup>1</sup> / <sub>2</sub>	37	33 <sup>1</sup> / <sub>2</sub>	39	29	41	31		
43	31	45	32 <sup>1</sup> / <sub>2</sub>	47	35	49	↓ 38 <sup>1</sup> / <sub>2</sub>	2	37 <sup>1</sup> / <sub>2</sub>	4	37				
6	44 <sup>1</sup> / <sub>2</sub>	8	48	10	48	12	36	14	35	16	33 <sup>1</sup> / <sub>2</sub>	18	31		
20	26 <sup>1</sup> / <sub>2</sub>	22	31	24	36	26	36	28	36	30					

TABLE 4. *Permanent exposure and de-radiation after 66 minutes.*

27	25 <sup>1</sup> / <sub>2</sub>	30	25 <sup>1</sup> / <sub>2</sub>	33	25 <sup>1</sup> / <sub>2</sub>	36	24	39	25 <sup>1</sup> / <sub>2</sub>	42	25 <sup>1</sup> / <sub>2</sub>	45	26	48	23
51	24	54	24	57	24	60	↑ 23 <sup>1</sup> / <sub>2</sub>	2	19	4	14 <sup>1</sup> / <sub>2</sub>	6	14 <sup>1</sup> / <sub>2</sub>	8	15 <sup>1</sup> / <sub>2</sub>
10	21 <sup>1</sup> / <sub>2</sub>	12	29	15	32	18	27	21	24	24	19	27	21 <sup>1</sup> / <sub>2</sub>	32	26 <sup>1</sup> / <sub>2</sub>
34	24	36	24	39	23	42	24	45	23	48	23	51	24	54	24
57	25	60	24	63	24	66	↓ 25	2	24	4	29	6	34	8	31 <sup>1</sup> / <sub>2</sub>
10	34	12	31	14	29	16	24	18	22 <sup>1</sup> / <sub>2</sub>	21	25 <sup>1</sup> / <sub>2</sub>	24	25 <sup>1</sup> / <sub>2</sub>	27	24
30	24	33	22 <sup>1</sup> / <sub>2</sub>	36	24	39	24	42							

TABLE 5. *Permanent exposure and de-radiation after 66 minutes.*

	27	28	31	29	33	30 <sup>1/2</sup>	36	29 <sup>1/2</sup>	39	28	42	27			
45	29 <sup>1/2</sup>	48	30 <sup>1/2</sup>	51	28	54	29	57	28	60	↑ 27	2	21 <sup>1/2</sup>		
4	17	6	19	8	29	10	31	12	33 <sup>1/2</sup>	14	35	16	31	18	24
21	22 <sup>1/2</sup>	24	30 <sup>1/2</sup>	27	32	30	30 <sup>1/2</sup>	33	27	36	24	39	24	42	29
45	30 <sup>1/2</sup>	48	28	51	26 <sup>1/2</sup>	54	29	60	26 <sup>1/2</sup>	63	26 <sup>1/2</sup>	66	↓ 27 <sup>1/2</sup>	2	29
4	31	6	31	8	33 <sup>1/2</sup>	10	31	12	22 <sup>1/2</sup>	14	23	16	24	18	21
21	24	25	24	27	21	30	24	33	24	36	25 <sup>1/2</sup>	39	25 <sup>1/2</sup>	42	25 <sup>1/2</sup>
44	25 <sup>1/2</sup>	50													

TABLE 6. *Permanent exposure and de-radiation after 114 minutes.*

36	38 <sup>1/2</sup>	38	36	40	38 <sup>1/2</sup>	42	38 <sup>1/2</sup>	44	39 <sup>1/2</sup>	46	40 <sup>1/2</sup>	48	38 <sup>1/2</sup>	
50	36	52	36	54	38 <sup>1/2</sup>	57	36	59	60	↑ 38 <sup>1/2</sup>	1	31 <sup>1/2</sup>	3	26 <sup>1/2</sup>
5	26 <sup>1/2</sup>	6	24	7	30	8	41	9	38 <sup>1/2</sup>	11	48	13	48	
15	47 <sup>1/2</sup>	17	44 <sup>1/2</sup>	19	39	22	45 <sup>1/2</sup>	24	35	27	33 <sup>1/2</sup>	29	38 <sup>1/2</sup>	
31	33 <sup>1/2</sup>	33	40 <sup>1/2</sup>	35	40 <sup>1/2</sup>	37	38 <sup>1/2</sup>	39	40 <sup>1/2</sup>	41	—	—	—	
—	—	—	—	90	41	92	38 <sup>1/2</sup>	94	41	96	41	98	39 <sup>1/2</sup>	
100	42	102	41	104	41	106	42	108	38 <sup>1/2</sup>	112	38 <sup>1/2</sup>	114	↓ 36	
2	38 <sup>1/2</sup>	4	47	6	51 <sup>1/2</sup>	8	55	10	50 <sup>1/2</sup>	12	41 <sup>1/2</sup>	14	42	
16	37 <sup>1/2</sup>	19	33 <sup>1/2</sup>	21	31	23	39 <sup>1/2</sup>	25	41 <sup>1/2</sup>	28	34 <sup>1/2</sup>	30	36	
32	33 <sup>1/2</sup>	34	33 <sup>1/2</sup>	36										

TABLE 7. *De-radiation after 110 minutes.*

—	—	—	60	27	63	26 <sup>1/2</sup>	66	26 <sup>1/2</sup>	69	29	72	27	75	25 <sup>1/2</sup>	78	28
81	26 <sup>1/2</sup>	84	27	87	26 <sup>1/2</sup>	90	27	93	29	96	29	99	28	102	27	
105	28	108	27	110	↓ 26 <sup>1/2</sup>	2	29	4	29	7	38 <sup>1/2</sup>	10	34 <sup>1/2</sup>	16	30 <sup>1/2</sup>	
19	29	22	26 <sup>1/2</sup>	25	26 <sup>1/2</sup>	28	28	31	24	34	28	37	25 <sup>1/2</sup>	40	25 <sup>1/2</sup>	
43																

TABLE 8. *De-radiation after 72 minutes.*

0	↑	—	—	—	30 <sup>1/2</sup>	—	—	—	60	29	62	32	67	31	68	30
72	↓	30	2	31	4	41	6	45	9	43	11	33 <sup>1/2</sup>	13	26 <sup>1/2</sup>		
15	31	18	36	20	32 <sup>1/2</sup>	22	27 <sup>1/2</sup>	24	25 <sup>1/2</sup>	22	(10 minutes delay)					
		37	29	38	31	42										

give instances. When after long exposure to radium the growth has become steady again, the radium-preparation cannot be removed without causing a new action contrary to the first. See fig. A', a continuation of figure A.

This response which is the result of the removal (eventually decrease) of radiation, we shall call the de-radiation-response for shortness' sake. In our experiments it became, quite unexpectedly a complete corroboration and

parallel of the *dark-growth-responses*, observed by TOLLENAAR (initially for *Avena sativa* already by SIERP) for various organs in a great number of experiments, as soon as a long exposure to light is stopped (eventually the intensity diminished). So the expression „de-radiation-response“ is very comprehensive. The dark-growth-response is one and we can distinguish it in the case of radium as radium-de-radiation-response.

### § 3. Short exposures.

#### Summarizing tables.

In the way described above cells were also exposed for a short period, but at 5 instead of 10 cms. distance, i.e. with an intensity about 4 times stronger. On exposure for 60 seconds there arises a violent undulatory reaction, instances of which are given in tables 9, 10 and 11, while the experiment of tab. 10 is represented in fig. B.

But a still shorter exposure, for about 5 sec. i.e. with twelve times slighter quantity shows a much fainter yet clearly perceptible radium-growth-response. See tables 12 and 13 and fig. C. Here the average growth-depression amounts to about 20 % at the lowest point.

Another typical difference with the light-growth-response appears; whereas in that case after fainter radiation, i.e. with a decreasing response, the beginning of the response is perceptibly later, this is certainly not the case in the experiments on exposure to radium hitherto made. The much fainter response after 5 sec. is certainly not later; it is perceptible in the rate of growth after about 2 minutes.

Attempting to draw a comparison of its strength with the light-growth-response, we should be careful not to take the 40 % retardation of growth quantitatively as the opposite of 40 % acceleration of growth. In the case of light accelerations of growth of e.g. 200 % are caused in these cells with

TABLE 9. 60 sec. Exposure at 5 cms. distance.

39	31	42	31	45	32	48	33 <sup>1</sup> / <sub>2</sub>	51	31	54	34	57	31
60	↕ 32	2	25 <sup>1</sup> / <sub>2</sub>	4	19	6	24	8	31	10	41	12	38 <sup>1</sup> / <sub>2</sub>
14	38 <sup>1</sup> / <sub>2</sub>	16	36	18	29	22	29	24	26 <sup>1</sup> / <sub>2</sub>	26	29	28	26 <sup>1</sup> / <sub>2</sub>
30	31	32	31	34	31	36	31	39	30	41	30	43	

TABLE 10. 60 sec. Exposure at 5 cms. distance.

44	31	46	30	48	31	50	31	52	33 <sup>1</sup> / <sub>2</sub>	54	32 <sup>1</sup> / <sub>2</sub>
56	33 <sup>1</sup> / <sub>2</sub>	58	33 <sup>1</sup> / <sub>2</sub>	60	↕ 33 <sup>1</sup> / <sub>2</sub>	2	21 <sup>1</sup> / <sub>2</sub>	4	17	5	19
6	24	8	35	10	43	12	44 <sup>1</sup> / <sub>2</sub>	14	42	16	39 <sup>1</sup> / <sub>2</sub>
18	33 <sup>1</sup> / <sub>2</sub>	20	30	22	29	24	24	26	32	28	32 <sup>1</sup> / <sub>2</sub>
30	33 <sup>1</sup> / <sub>2</sub>	32	38 <sup>1</sup> / <sub>2</sub>	34	35	36	35	38	33 <sup>1</sup> / <sub>2</sub>	40	31
42	31	44	32 <sup>1</sup> / <sub>2</sub>	46	35	48	36	50	35	52	

TABLE 11. 60 sec. Exposure at 5 cms. distance

37	31	39	33 $\frac{1}{2}$	41	32 $\frac{1}{2}$	43			33 $\frac{1}{2}$	47	33 $\frac{1}{2}$	49	32	
52	30 $\frac{1}{2}$	54	31	56	32 $\frac{1}{2}$	58	31	60	↑	33 $\frac{1}{2}$	2	29	4	<b>24</b>
6	27 $\frac{1}{2}$	8	35	10	35	12	<b>43</b>	14		<b>41</b>	16	37	18	38 $\frac{1}{2}$
20	33 $\frac{1}{2}$	22	29	24	30	27	31	29		32 $\frac{1}{2}$	31	33 $\frac{1}{2}$	33	33 $\frac{1}{2}$
35	33 $\frac{1}{2}$	37												

TABLE 12. 5 sec. Exposure at 5 cms. distance.

38	38 $\frac{1}{2}$	40	36	42	37	44	35 $\frac{1}{2}$	48	38 $\frac{1}{2}$	51	36	53	38 $\frac{1}{2}$	
56	36	58	36	60	↑	36	2	31	4	<b>29</b>	5	<b>29</b>	6	<b>29</b>
7	38 $\frac{1}{2}$	8	<b>43</b>	9	<b>43</b>	10	38 $\frac{1}{2}$	12	41	14	41	16	36	
18	37	20	31	22	36	24	33 $\frac{1}{2}$	26	41	29	38 $\frac{1}{2}$	31	41	
33	36	35	36	37										

TABLE 13. 5 sec. Exposure at 5 cms. distance.

42	27 $\frac{1}{2}$	44	27 $\frac{1}{2}$	46	26 $\frac{1}{2}$	48	26 $\frac{1}{2}$	50	26 $\frac{1}{2}$	52	27 $\frac{1}{2}$	54	27	
56	26 $\frac{1}{2}$	58	27 $\frac{1}{2}$	60	↑	29	2	24	3	21 $\frac{1}{2}$	4	24	5	24
6	24	7	29	8	31	9	31 $\frac{1}{2}$	11	33 $\frac{1}{2}$	13	31	14	29	
15	29	16	29	17	29	18	26 $\frac{1}{2}$	20	27 $\frac{1}{2}$	22	29	24	27 $\frac{1}{2}$	
26	26 $\frac{1}{2}$	28	29	30	27 $\frac{1}{2}$	32	25	34	26 $\frac{1}{2}$	36	26 $\frac{1}{2}$	38	27 $\frac{1}{2}$	
40														

small light-doses, whereas conversely a retardation of growth would have its maximum at 100 %, i.e. arrest if growth.

On the whole a retardation of growth indicates a stronger internal action than an acceleration of growth of equal percentage, especially according as the retardation (resp. acceleration) indicates a higher percentage. With the responses of growth an acceleration of 100 % is by no means quantitatively the reverse of 100 % retardation. The fainter the responses, the nearer we approach the limit of response, the better we can compare a positive and a negative response. Bearing this argument in mind, we may draw an approximate comparison for the following weak responses.

The radium-growth-response called forth by this preparation at 5 cms. distance for 5 sec. causes a retardation of growth of about 20 %, an exposure to  $\frac{1}{4}$  M.K.S., 4-sided an acceleration up to about 20 %. Considering that the limit of a perceptible light-growth-response ("threshold") lies at about  $\frac{1}{100}$  M.K.S., i.e. 25 times lower, the limit of the radium-growth-response will lie at about  $\frac{1}{5}$  sec. under the circumstances described.

For comparison of light-growth-response and radium-growth-response a summarizing table follows. For comparison with 60 sec. radium-exposure, the results are used of radiations (4-sided) with light of 4 M.K.S., whilst in fig. E one of those experiments has been represented according to the figures found in 1913—1914.

TABLE 14. Comparison of light- and radium-growth-responses after short exposures, at 17° C.

	Average beginning of growth-response after at least	Maximum of response averagely	Maximum of response averagely after
4 M. K. S. 4-sided	3½ minutes	55 % +	7 minutes
9½ mgrs. Ra-element at 5 cms. distance for 60 sec.	2 minutes	40 % -	5½ minutes
¼ M. K. S. 4-sided	8½ minutes	ca 20 % +	11 minutes
9½ mgrs. Ra-element at 5 cms. distance for 5 sec.	2 minutes	ca 20 % -	5 minutes

From the experiments hitherto made, nearly all rendered in the above tables, we summarize the cardinal points about period and strength of response in the tables 15, 16, 17 and 18.

TABLE 15.

Beginning decrease rate of growth in the period:	Minimum rate of growth	Maximum rate of growth (anti-reaction)	2nd Minimum
Permanent exposure	3-6 Min.	3-9 Min.	18-19 Min.
	3-6	3-6	12-15
	2-5	2-5	20-23
	2-4	4-8	15-18
	2-4	4-6	14-16
	0-2	4-6	13-15
	1-3	5-7	13-15
60 sec.	2-4	4-6	10-12
	2-4	4-5	12-14
	2-4	4-6	12-14
5 sec.	2-4	4-7	8-10
	2-3	3-4	11-13
	1-3	5-7	-

TABLE 16.

De-radiation after :	Beginning increase rate of growth in the period	Maximum rate of growth	Minimum rate of growth
49 Min..	?	8—12 Min.	20—22 Min.
66	4—6 Min.	6—12	—
66	?	8—10	18—21
72	4—6	6—11	13—15
110	7—10	7—10	—
114	4—6	8—10	21—23
159	3—6	6—10	—

TABLE 17.

	Decrease rate of growth 1st minimum	Increase rate of growth in maximum
Permanent exposure	35 per ct.	45 per ct.
	50	33
	40	33
	42	21
	40	33
	36	26
60 sec.	40	28
	48	33
	25	32
5 sec.	21	16
	22	22

TABLE 18.

De-radiation after	Increase rate of growth in maximum	Decrease rate of growth in minimum
49 Min.	33 per ct.	26 per ct.
66	41	6?
66	22	22
72	50	12
110	43	—
114	45	18

In connection with tables 14—18 we draw the attention to the following facts: 1. that the growth-responses are undulatory, the undulation gradually settling down into a steady growth, 2. that weak radium-growth-responses (in short exposures) do certainly not begin later as is the case with the light-growth-responses (see esp. table 14), 3. that the response to de-radiation undoubtedly begins a little later and reaches its maximum later than the response to radiation, exactly as was found in the case of the dark-growth-response.

§ 4. *Is the perception of light- and gamma-rays of a different nature?*

One principal question was most urging. Are light-growth-response and the response to gamma-rays, though contrary, yet identical as to their influence on the cell? For instance will organs, which contrary to *Phycomyces* show a negative light-growth-response, also respond contrary to *Phycomyces* as to the radium-growth-response? Or will all organs show a parallel response to gamma-rays? First the roots of *Sinapis alba* were exposed to rays at 5 cms. distance for 4 minutes. In spite of an extremely regular growth there was not the least indication of a radium-growth-response. But after all, this might very well be, though there was a relation between the influences of light- and gamma-rays. For the roots of *Sinapis* respond faintly to light; according to previous data they are at least 100.000 times less sensitive than *Phycomyces*-cells. For that reason the experiments were continued with *Helianthus*-germ-plants, which are at least 1000 times more sensitive to light. Here too the growth was extremely regular and could be accurately observed. The observations were continued for hours at a stretch. Nor was a trace of radium-growth-response to be found here.

On our considering the values previously found, we find that in *Helianthus* 4 M.K.S. causes a decrease of growth of not yet 10 %, 32 M.K.S. of averagely 23 %, in *Phycomyces*  $\frac{1}{4}$  M.K.S. an increase of growth of about 20 % : 32 M.K.S. of 75 %. For *Helianthus* we approach with 4 M.K.S. the limit lying at about  $\frac{1}{1000}$  M.K.S. for *Phycomyces*. From these data we may conclude that roughly estimated the *Phycomyces*-cell needs about  $\frac{1}{100}$  part of the light necessary for the *Helianthus*-germ-plant to give still a visible response; *Helianthus* therefore is about 80—100 times less sensitive to light than *Phycomyces*. The possibility remains, that on exposure to a much greater quantity of radium these germ-plants might show a directly perceptible response in their rate of growth. It may also be, that their non-reaction is due to quite different a mode of perception of light- and gamma-rays. On this subject the following experiments have been made.

Meanwhile the tables of *Helianthus* and *Sinapis* with perfectly even growth are left out for shortness' sake.

We know that the sensitiveness to light of the *Phycomyces*-cells in the dark is very great, but that it strongly decreases, when these cells are exposed (4-sided) to a constant, permanent intensity for a long period of time. The quantity of light which was to be supplied to cause a response of growth increases enormously, according as the intensity to which the cells are adapted, increases. While this limit lies in the dark at about 0.01 M.K.S., at 1 M.K. it has already risen to 25—50, at 8 M.K. to 200—400 MK.S.

Now let us put our cells for some hours in 4 M.K., then the sensitiveness is 10 to 20 thousand times slighter than in the dark.

As described and represented above the radium-growth-response at 5 cms. distance for 60 sec. was very vigorous. That is a radiation, which according

to our above statement, is but about 300 times greater than the limit (ca  $\frac{1}{5}$  sec.), at which a response would be barely perceptible. It is true that light and radium-growth-response are opposed, but it might be possible, that the perception, the initial influence of these rays was of identical character.

If the sensitiveness to radium has decreased as enormously, as the sensitiveness to light in 4 M.K., the exposure for 60 sec. (ca 300 times the limit in dark) would be absolutely insufficient to cause a response. Seeing the two reactions are opposed, it might be that after the diminution of light-sensitiveness, the possibility of radium-response might be greatly increased. They are all suppositions, only to be answered by experiments.

Tables 19, 20 and 21 refer to experiments, in which the cells were permanently exposed 4-sided to 4 M.K. and after  $3\frac{1}{2}$ , and  $4\frac{1}{2}$  hours moreover to the radium-preparation at 5 cms. distance for 60 seconds. To attain this another card-board house was constructed with 4 mirrors in the corners for the lateral radiation of the cell with light from a 4-volt lamp. As on account of the mirrors the house had to be larger than in the previous experiments, there was made in the middle of the side-wall (for the sake of symmetry in both side-walls) a re-entering angle, to enable us to keep the preparation (and the interposed filters) outside the house, yet at 5 cms. distance from the cell.

*With an illumination of 4 M.K., 4-sided, the sensitiveness to light being made 10.000 times slighter, the radium-growth-response continues the same.*

Figure D pictures one of the 3 tables with the radium-growth-response in a intensity of 4 M.K., 4-sided. This figure D is directly comparable with figure B of the same response to radiation in the dark.

It is very probable that the initial influence of the light-rays and the gamma-rays (i.e. the perception of those rays viewed from the side of the plant-cell) is of quite a different nature or at least touches quite different a link of the process of metabolism. Only secondarily the results of both are shown in the modifications of the rate of growth described above.

TABLE 19. *Exposed to 4 M.K. 4-sided. After  $3\frac{1}{2}$  hours 60 sec. Ra-exposure at 5 cms. distance*

24	$32\frac{1}{2}$	28	36	32	34	36	$33\frac{1}{2}$	38
	36	40	37	44	$33\frac{1}{2}$	47	35	50
	36	53	$33\frac{1}{2}$	56	35	59	(0↑)	32
2	<b>23</b>	4	<b>24</b>	6	36	8	<b>42</b>	10
	<b>41</b>	12	<b>41</b>	14	<b>42</b>	16	36	18
	$33\frac{1}{2}$	20	$33\frac{1}{2}$	22	31	24	32	28
	$33\frac{1}{2}$	31	$33\frac{1}{2}$	34	35	87	$30\frac{1}{2}$	40
	$30\frac{1}{2}$	43	29	46	32	49	32	52
	32	55	32	58	$33\frac{1}{2}$	61	35	64
	$34\frac{1}{2}$	67	32	70	$30\frac{1}{2}$	73	32	76
	$33\frac{1}{2}$							



TABLE 23. *Exposed to 4 M.K. 4-sided, for 5 hours next darkness.*

0	33 <sup>1</sup> / <sub>2</sub>	2	33 <sup>1</sup> / <sub>2</sub>	4	31	6	32	8	33 <sup>1</sup> / <sub>2</sub>	10	33 <sup>1</sup> / <sub>2</sub>	13
	35	16	30 <sup>1</sup> / <sub>2</sub>	19	30 <sup>1</sup> / <sub>2</sub>	22	29	25	32	28	32	31
	32	34	32	37	33 <sup>1</sup> / <sub>2</sub>	40	35	43	34	46	32	49
	30 <sup>1</sup> / <sub>2</sub>	52	32	55	33 <sup>1</sup> / <sub>2</sub>	0 ↓	33 <sup>1</sup> / <sub>2</sub>	2	32 <sup>1</sup> / <sub>2</sub>	4	31	6
	31	8	23	10	<b>18</b>	12	<b>18</b>	10	<b>18</b>	16	19	18
	18 <sup>1</sup> / <sub>2</sub>	20	18 <sup>1</sup> / <sub>2</sub>	23	<b>14</b> <sup>1</sup> / <sub>2</sub>	26	19	29	27	32	22 <sup>1</sup> / <sub>2</sub>	35
	19	38	<b>24</b>	41	30 <sup>1</sup> / <sub>2</sub>	44	35	47	28	50	21 <sup>1</sup> / <sub>2</sub>	53
	17 <sup>1</sup> / <sub>2</sub>	56	25 <sup>1</sup> / <sub>2</sub>	59	36	62	32	65	29	68	33 <sup>1</sup> / <sub>2</sub>	71
	32	74	29 <sup>1</sup> / <sub>2</sub>	77	27	80	27	83	28	86		

In these latter experiments we availed ourselves of the opportunity to withdraw the light-rays from the cells, which had been exposed for 5 and 6 hours to 4 M.K., after recovering from the 60 sec. Ra-exposure. In the experiments of tables 22 and 23 and in figure F (with a continuation F') a repeated corroboration may be found of a vigorous *dark-growth-response* after the growth has been adapted to a constant supply of light.

It stands to reason that here we have only just touched upon the subject of this striking radium-growth-response. Many new questions have arisen, into which the investigations should be continued. This narrow compass does not allow of discussing the question whether a comparison with other known physiological results of similar exposures is possible. This however is certain and may be important for human physiology and therapy, that the growth of these cells is an extremely sensitive measure or indicator for judging a physiologic effect of the gamma-rays and may be of other rays and thus for the quantitative comparison of such radiations different in intensity, in distance, in time, continuous or intermittent.

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**Physics.** — “*The Intensities of the ZEEMAN-Components*”<sup>1)</sup>. By S. GOUDSMIT and R. DE L. KRONIG. (Communicated by Prof. P. EHRENFEST).

(Communicated at the meeting of February 28, 1925).

By the aid of the correspondence-principle formulae have been given by SOMMERFELD and HEISENBERG<sup>2)</sup> for the intensities of the ZEEMAN-components for the case of large quantum numbers. These formulae have been expressed in the quantum numbers by LANDÉ<sup>3)</sup>.

If for the initial state the quantum numbers considered here are  $J_1$  and  $m_1$ , for the final state  $J_2$  and  $m_2$ , the formulae for transversal observation are:

For the case that  $J_2 = J_1 + 1$

$$\left. \begin{aligned} m_2 = m_1 + 1 & \quad i_+ = A(\bar{J} + \bar{m})(\bar{J} + \bar{m}), \sigma \\ m_2 = m_1 & \quad i_0 = 4A(\bar{J} + \bar{m})(\bar{J} - \bar{m}), \pi \\ m_2 = m_1 - 1 & \quad i_- = A(\bar{J} - \bar{m})(\bar{J} - \bar{m}), \sigma \end{aligned} \right\} \dots \dots (1)$$

For the case that  $J_2 = J_1$

$$\left. \begin{aligned} m_2 = m_1 + 1 & \quad i_+ = B(\bar{J} + m)(\bar{J} - \bar{m}), \sigma \\ m_2 = m_1 & \quad i_0 = 4B\bar{m}^2, \pi \\ m_2 = m_1 - 1 & \quad i_- = B(\bar{J} + \bar{m})(\bar{J} - \bar{m}), \sigma \end{aligned} \right\} \dots \dots (2)$$

in which  $\bar{J}$  and  $\bar{m}$  express that it is uncertain whether in these formulae the quantum numbers of the initial or of the final state, or of an intermediate mode of motion should be used.

ORNSTEIN and BURGER<sup>4)</sup> drew up the rule that the energy emitted by one of the magnetic levels of the initial state towards the final state, is equal for all these levels, on account of the equal-probability of the levels in a magnetic field. The same thing will hold for the energies which arrive at the magnetic levels of the final state. For the application

<sup>1)</sup> Preliminary communication in *Naturwiss.* **13**, 90, 1925.

H. HÖNL. arrives independently at the same results in *ZS. f. Phys.* **31**, 340, 1925. Cf. also an article by R. DE L. KRONIG, which will shortly be published in *ZS. f. Phys.*

<sup>2)</sup> A. SOMMERFELD and W. HEISENBERG *ZS. f. Phys.* **11**, 131, 1922.

<sup>3)</sup> BACK-LANDÉ. *ZEEMANEFFECT u. Multiplettstruktur* p. 52.

<sup>4)</sup> L. S. ORNSTEIN and H. C. BURGER. *ZS. f. Phys.* **28**, 135 and **29**, 241, 1924.

of this rule it should be borne in mind that in the transversal observation only half the energy of the circularly polarized components finds expression. Hence ORNSTEIN and BURGER'S rule gives:

$$2i_+ + i_0 + 2i_- = C \dots \dots \dots (3)$$

It seemed now natural to examine whether this relation, in connection with the formulae (1) and (2), might possibly be able to yield the intensities also for small quantum numbers. For this purpose different methods may be adopted, one of which will be discussed in what follows.

In connection with formulae (1) and (2) it will be expected that for small quantum numbers for  $J_2 = J_1 + 1$

$$\left. \begin{aligned} m_2 = m_1 + 1 \quad i_+ &= A(J_1 + m_1 + a_1)(J_1 + m_1 + a_2) = A(m_1^2 + a_1 m_1 + a_2) \\ m_2 = m_1 \quad i_0 &= -4A(J_1 + m_1 + b_1)(J_1 + m_1 + b_2) = -4A(m_1^2 + \beta_1 m_1 + \beta_2) \\ m_2 = m_1 - 1 \quad i_- &= A(J_1 + m_1 + c_1)(J_1 + m_1 + c_2) = A(m_1^2 + \gamma_1 m_1 + \gamma_2) \end{aligned} \right\} (4)$$

In these formulae the intensities are expressed in the quantum numbers of the initial state, whereas the constants  $a, \beta, \gamma$  are independent of  $m$ . If we fill in the last members of these expressions in (3), and if we require the result to be independent of  $m$ , then

$$a_1 - 2\beta_1 + \gamma_1 = 0 \dots \dots \dots (5)$$

If in fig. 1, where the case  $J_1 = J_2 + 1$  is diagrammatically represented, the virtual components on the edge of the scheme are considered, then

$$\begin{aligned} i(p) &= A \{ (J_1 + 1\frac{1}{2})^2 + \gamma_1 (J_1 + 1\frac{1}{2}) + \gamma_2 \} = 0 \\ i(q) &= A \{ (J_1 + \frac{1}{2})^2 + \gamma_1 (J_1 + \frac{1}{2}) + \gamma_2 \} = 0 \end{aligned}$$

from which follows

$$\underline{\gamma_1 = -2(J_1 + 1)} \quad \underline{\gamma_2 = (J_1 + \frac{1}{2})(J_1 + 1\frac{1}{2})}$$

In the same way it is found that

$$\begin{aligned} i(\bar{p}) &= A \{ (J_1 + 1\frac{1}{2})^2 - a_1 (J_1 + 1\frac{1}{2}) + a_2 \} = 0 \\ i(\bar{q}) &= A \{ (J_1 + \frac{1}{2})^2 - a_1 (J_1 + \frac{1}{2}) + a_2 \} = 0 \end{aligned}$$

hence

$$\underline{a_1 = 2(J_1 + 1) = -\gamma_1} \quad \underline{a_2 = (J_1 + \frac{1}{2})(J_1 + 1\frac{1}{2}) = \gamma_2}$$

The result  $a_1 = -\gamma_1$  and  $a_2 = \gamma_2$  might already have been arrived at from the symmetry of the ZEEEMAN resolutions. With (5) this yields

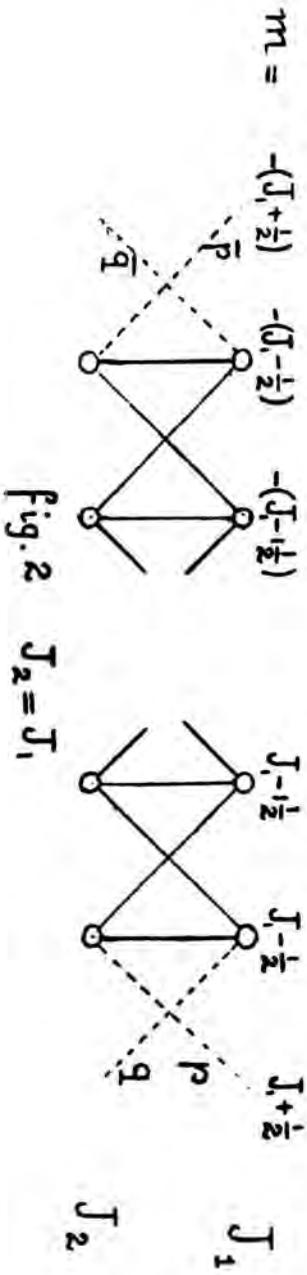
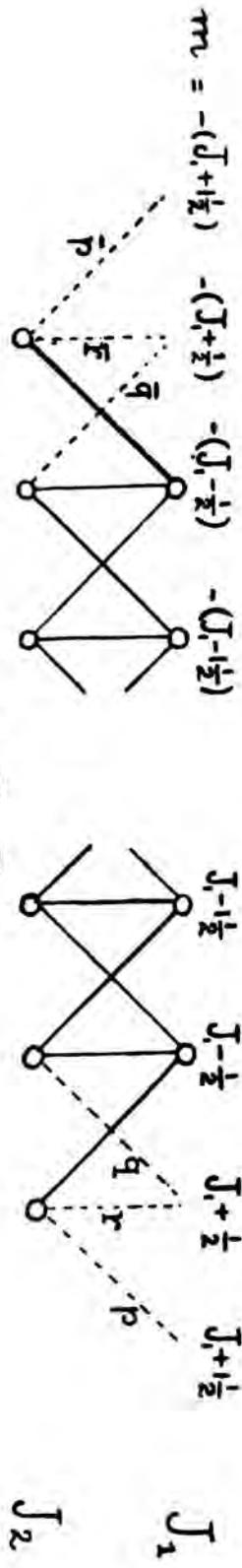
$$\underline{\beta_1 = 0}$$

Finally

$$i(r) = -4A \{ (J + \frac{1}{2})^2 + \beta_2 \} = 0$$

yields

$$\underline{\beta_2 = -(J + \frac{1}{2})^2}$$



The final formulae are therefore:

$$\begin{aligned} i_+ &= A \{ m_1^2 + 2(J+1)m_1 + (J_1 + \frac{1}{2})(J_1 + 1\frac{1}{2}) \} \\ i_0 &= -4A \{ m_1^2 - (J + \frac{1}{2})^2 \} \\ i_- &= A \{ m_1^2 - 2(J+1)m_1 + (J_1 + \frac{1}{2})(J_1 + 1\frac{1}{2}) \}. \end{aligned}$$

These formula may also be written symmetrically in the quantum numbers of the initial and final states to bring them in agreement with the formulae (1):

$$J_2 = J_1 + 1 \begin{cases} i_+ = A(J_1 + \bar{m})(J_2 + \bar{m}) = A(\bar{J} + m_1)(\bar{J} + m_2) \\ i_0 = 4A(\bar{J}^2 - \bar{m}^2) = 4A(\bar{J} + \bar{m})(\bar{J} - \bar{m}) \\ i_- = A(J_1 - \bar{m})(J_2 - \bar{m}) = A(\bar{J} + m_1)(\bar{J} - m_2) \end{cases}$$

in which  $\bar{J}$  and  $\bar{m}$  now represent the arithmetical means between the initial and final states. It may also still be shown that these formulae satisfy the condition that the sum of the intensities of the  $\sigma$ -components is equal to that of the  $\pi$ -components.

The same procedure is followed in the case that  $J_2 = J_1$ . Then according to fig. 2:

$$\begin{aligned} i(p) &= -B \{ (J_1 + \frac{1}{2})^2 + \gamma_1 (J_1 + \frac{1}{2}) + \gamma_2 \} = 0 \\ i(\bar{q}) &= -B \{ (J_1 - \frac{1}{2})^2 - \gamma_1 (J_1 - \frac{1}{2}) + \gamma_2 \} = 0 \end{aligned}$$

from which

$$\underline{\gamma_1 = -1} \quad \underline{\gamma_2 = -(J_1 + \frac{1}{2})(J_1 - \frac{1}{2})}.$$

Likewise

$$\begin{aligned} i(q) &= -B \{ (J_1 - \frac{1}{2})^2 + a_1 (J_1 - \frac{1}{2}) + a_2 \} = 0 \\ i(\bar{p}) &= -B \{ (J_1 + \frac{1}{2})^2 - a_1 (J_1 + \frac{1}{2}) + a_2 \} = 0, \end{aligned}$$

from which

$$\underline{a_1 = 1 = -\gamma_1} \quad \underline{a_2 = -(J_1 + \frac{1}{2})(J_1 - \frac{1}{2}) = \gamma_2}.$$

This combined with (5) gives:

$$\underline{\beta_1 = 0}.$$

The simplest way to determine  $\beta_2$  is now by making use of the fact that in this case for:

$$m_1 = m_2 = 0 \quad , \quad i_0 = 0$$

or, what is more complicated, by requiring the total intensity of the  $\sigma$ -components to be equal to that of the  $\pi$ -components. Then we find:

$$\underline{\beta_2 = 0}.$$

Hence for the case  $J_2 = J_1$  the formulae become:

$$\begin{aligned} i_+ &= -B \{ m_1^2 + m_1 - (J_1 + \frac{1}{2})(J_1 - \frac{1}{2}) \} \\ i_0 &= 4B m_1^2 \\ i_- &= -B \{ m_1^2 - m_1 - (J_1 + \frac{1}{2})(J_1 - \frac{1}{2}) \} \end{aligned}$$

or written symmetrically:

$$J_2 = J_1 \begin{cases} i_+ = B(\bar{J} + \bar{m})(\bar{J} - \bar{m}) \\ i_0 = 4B\bar{m}^2 \\ i_- = B(\bar{J} + \bar{m})(\bar{J} - \bar{m}). \end{cases}$$

In both cases the same results may also be obtained, but in a more lengthy way, by carrying out the calculations with the real components at the edges of the schemes.

*Leiden, Instituut voor theoretische Natuurkunde.*

**Chemistry.** — "On the Pseudo-symmetry of Racemic Potassium Chloro-sulfoacetate." By Prof. F. M. JAEGER.

(Communicated at the meeting of May 30, 1925).

The crystalform of racemic *potassium-chloro-sulfoacetate*, whose constitution is:  $\left. \begin{array}{l} \text{CHCl} \cdot \text{SO}_3\text{K} \\ | \\ \text{COOK} \end{array} \right\}_2 + 3 \text{H}_2\text{O}$ , has not been well known up till now.

RATHKE<sup>1)</sup> concluded from his measurements that the compound must be considered to be tetragonal, while DOELTER<sup>2)</sup> described the substance as possessing rhombic symmetry, as a result of very insufficient data obtained by him with evidently badly developed crystals. These showed a combination of a rhombic bipyramid  $\{111\}$  and the basis  $\{001\}$ ; the angle  $(111):(111)$  was found to have values ranging from  $85^\circ$  to  $88^\circ$ , while for the angle  $(001):(111)$  values are given oscillating between  $68^\circ$  and  $72^\circ$ .

Prof. BACKER was so kind as to put at my disposal some crystals, which he obtained by slow evaporation from aqueous solutions containing also *potassium bromide*. These beautiful crystals appeared to be perfectly clear and to possess perfectly plane, lustrous faces; moreover they showed optical properties of a very particular character, which invited to closer examination. The results obtained during this investigation are here recorded.

The salt crystallizes most frequently in the shape of thin square plates and sometimes also as thick quadratic crystals which are truncated at two opposite corners (Fig. 1). The faces of these crystals were in all cases highly lustrous; the angular values in separate individuals appeared to be very constant, accurate measurements being therefore possible here.

The symmetry is apparently rhombic-bipyramidal, with a very close approximation to tetragonal symmetry; the geometrical form may, therefore, be safely described as pseudo-tetragonal. This fact, which finds its expression also in the values of the crystal-parameters:

$$a : b : c = 0.9973 : 1 : 2.7650$$

explains at the same time the discordant results of the measurements of the earlier observers mentioned above.

*Observed forms*:  $c = \{001\}$ , always strongly predominant and highly lustrous; on microscopical observation the faces of this form show a very fine striation parallel to the edge  $(001):(101)$ .

<sup>1)</sup> B. RATHKE, Lieb. Ann. der Chemie, **161**, 166, (1872).

<sup>2)</sup> C. DOELTER, Sitzber. d. Akad. d. Wiss. Wien, **93**, II, 685, (1886); Monatshefte **7**, 159.

Moreover:  $\omega = \{111\}$  and  $o = \{113\}$ , both sometimes equally broad, but in most cases  $\omega$  appreciably broader than  $o$ ; the planes of  $\omega$  give also much better reflections than  $o$ , the faces of this latter form being usually finely striated parallel to the edge  $(001):(111)$ . The bigger and

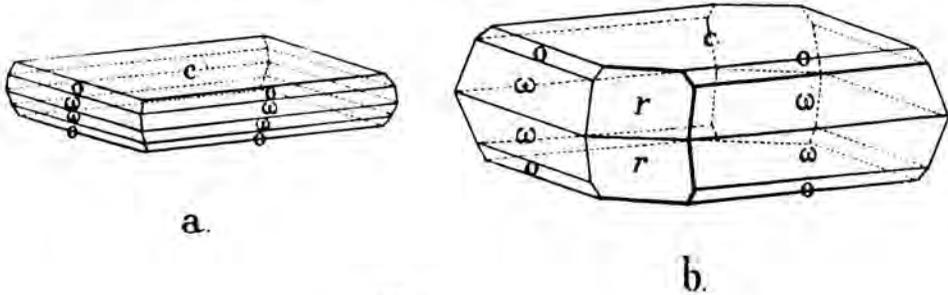


Fig.1

thicker individuals show, moreover, the form  $r = \{101\}$ , which has also very lustrous faces, yielding very sharp reflexion-images. The plane angles on  $\{001\}$  are  $89^\circ 48'$ , resp.  $90^\circ 12'$ ; the faces of  $\{001\}$  and in the same way the opposite faces of  $\{113\}$  are never completely parallel, but deviate from parallel orientation about  $10'$ .

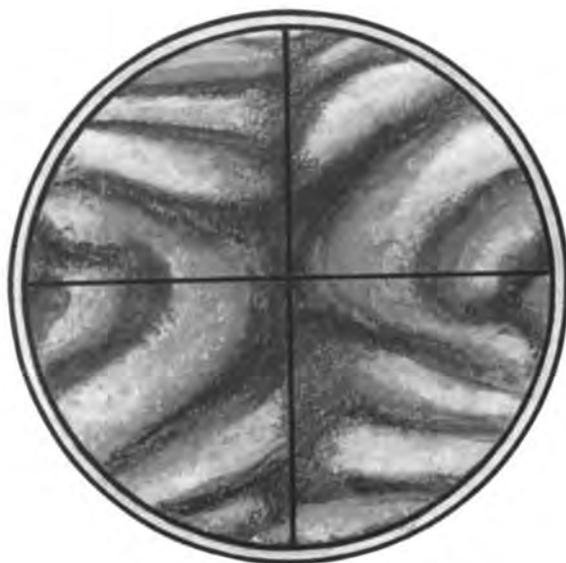
Doubtlessly this fact is connected with the rather complicated structure of the crystals explained in the following.

Angular Values:	Observed:	Calculated:
$c : \omega = (001) : (111) =^* 75^\circ 40\frac{1}{2}'$		—
$c : r = (001) : (101) =^* 70 10\frac{1}{2}'$		—
$c : o = (001) : (113) = 52 34$		$52^\circ 33'$
$o : \omega = (113) : (111) = 23 6\frac{1}{2}'$		$23 7\frac{1}{2}'$
$\omega : \omega = (111) : (\bar{1}\bar{1}\bar{1}) = 28 39$		$28 39$
$o : o = (113) : (\bar{1}\bar{1}\bar{3}) = 68 36$		$68 26$
$\omega : \omega = (111) : (\bar{1}\bar{1}\bar{1}) = 86 37$		$86 18$
$\omega : \omega = (111) : (\bar{1}\bar{1}\bar{1}) = 86 21$		$86 41$
$o : o = (113) : (\bar{1}\bar{1}\bar{3}) = 68 25$		$68 10$
$r : r = (101) : (101) = 39 39$		$39 39$

The crystals show a good cleavage parallel to  $\{001\}$ .

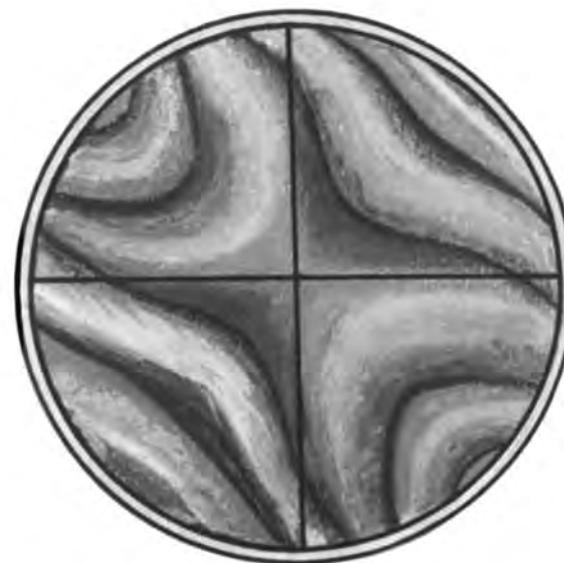
#### Optical Properties.

In parallel polarized light the crystals show diagonal extinction on  $\{001\}$ . However, they clearly possess a zonal structure: generally there is a central, quadratically limited field, which is divided into four quadrants separated by boundary-lines parallel and perpendicular to the edge  $c:r$ . The pairs of opposed quadrants have always the same optical orientation. Round this central part successive zones are arranged,



a.  
Normal Position  
(Axial plane horizontally orientated)

Fig. 2



b.  
Diagonal Position

RACEMIC POTASSIUM-CHLOROSULFOACETATE

which go parallel to the boundaries of the square plates; these zonal bands appear to get thinner, as they approach the circumference of the crystal-plates. The plane of the optical axis for yellow light in each band is parallel to  $\{100\}$ ; the direction of the  $c$ -axis is that of the first bisector, with negative optical character.

In convergent polarized light one observes a strangely shaped interference-image (Fig 2<sup>a</sup>), if the principal sections of the Nicol's prism are parallel to the diagonals of (001). When the crystal is turned over 45°, the interference-image is that represented in Fig. 2<sup>b</sup>; there are no branches of a dark hyperbola present. The axial image of Fig. 2<sup>a</sup> is evidently only *centrically*-symmetrical: it shows an extremely strong *crossed* dispersion of monoclinic character, with  $\rho < \nu$ .

From this it follows that the structure is only rhombic in appearance; in reality it is monoclinic. By an almost perpendicular crossing of monoclinic lamellae a polysynthetic twin-structure is created, which very closely imitates a pseudo-rhombic, and almost tetragonal regularity. To this intergrowth of monoclinic lamellae correspond as well the fine striations on the faces of  $\{001\}$  and  $\{113\}$ , as the irregularities of the architecture of the crystals, as they are revealed by the more significant oscillations of the angular values in the zone of the edge (001):(101) caused by the want of parallelism between (001) and (00 $\bar{1}$ ). It was impossible to intensify the lamellar appearance of the crystals by heating, because the crystals on heating very soon show numerous bursts and then get turbid and opaque by deshydration.

The pseudo-symmetrical character of the crystals thus being established beyond all doubt, suspicion arises that the salt is no racemate in the proper sense of the word, but rather a pseudo-racemic intergrowth of 50% of the right- and lefthanded antipodes. Certainty about this could only be obtained, if it were possible to compare the crystalforms of the optically active components separately with that of the salt described. However, this experiment remains unrealisable as a consequence of the fact that the potassium-salts of the optically-active chloro-sulfoacetic acids are very rapidly racemized in solution, it being, therefore, impossible to get measurable crystals of both components in a pure state.

*Laboratory for Inorganic and  
Physical Chemistry of the University.*

Groningen, (Netherlands), May 1925.

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**Botany.** — „Ueber die Gültigkeit des Sinusgesetzes für die geotropische Reizung von *Avena-Koleoptilen* bei kleinen Ablenkungswinkeln.“  
Von Dr. ERICH SCHNEIDER. (Communicated by Prof. F. A. F. C. WENT.)

(Communicated at the meeting of June 27, 1925).

Die Untersuchungen von RUTTEN—PEKELHARING über die Perzeption des Schwerkraftreizes<sup>1)</sup> haben bewiesen, dass für die geotropische Reizung von Koleoptilen von *Avena sativa* und Wurzeln von *Lepidium sativum* das Produktgesetz (Reizintensität  $\times$  Reizdauer = konstant) Gültigkeit hat, wenn die Neigung, bei der die geotropische Reizung erfolgt, eine nicht zu geringe Ablenkung von der Vertikalen bedeutet, d.h. die Neigungswinkel nicht unter etwa 20° oder über 170° gross waren.

Es schien wahrscheinlich, dass diese Abweichungen, die sich bei der Reizung bei kleinen Ablenkungswinkeln gezeigt hatten, sich als Versuchsfehler herausstellen dürften, wenn es gelänge, die Untersuchungsmethoden entsprechend zu verfeinern.

Durch Vermittlung von Herrn Professor KÜSTER, dem ich hierfür auch an dieser Stelle Dank sagen darf, hatte ich Gelegenheit, in den Monaten März und April 1925 am botanischen Laboratorium der Universität Utrecht Untersuchungen über die angeregte Frage anzustellen. Meine Aufgabe bestand darin, zu prüfen, inwieweit sich mit den inzwischen sehr verfeinerten Methoden die Gültigkeit des Produktgesetzes für Avenakoleoptilen für die geotropische Reizung bei kleinen Ablenkungswinkeln ebenso befriedigend bestätigen liesse, wie es bei Wurzeln von *Lepidium sativum* schon RUTTEN—PEKELHARING<sup>2)</sup> und später auch TRÖNDLE<sup>3)</sup> gelungen war, der mit genaueren Methoden arbeiten konnte.

Den Gültigkeitsnachweis für das Produktgesetz bei kleinen Ablenkungswinkeln versuchte ich durch Bestimmung der Präsentationszeit bei den verschiedenen Neigungswinkeln zu erbringen und durch die Nachprüfung, inwieweit die gefundenen Präsentationszeiten mit den errechneten übereinstimmten. Grundlage für die Berechnung der Präsentationszeiten war die von mir in zahlreichen Versuchen ermittelte Präsentationszeit für 90° Ablenkung. Betrug diese  $x$  Sekunden, so errechnete sich die Präsentationszeit für andere Winkel hieraus durch Multiplikation von  $x$  mit dem Sinus des Ablenkungswinkels  $\alpha$  (Präsentationszeit =  $x \sin. \alpha$ ).

Die Methode nach der ich meine Versuche anstellte war die folgende: Zu den Versuchen wurden Früchte der reinen Linie „Siegshafer“ ver-

<sup>1)</sup> RUTTEN—PEKELHARING, C. J.: Untersuchungen über die Perzeption des Schwerkraftreizes (Rec. d. trav. bot. Néerl. 7, 1910, 241).

<sup>2)</sup> RUTTEN—PEKELHARING: a. a. O., 278.

<sup>3)</sup> TRÖNDLE, A.: Untersuchungen über das Sinusgesetz bei den geotropischen Reaktionen von *Lepidium* (Jahrb. f. wiss. Bot. 60, 1921, 295).

wandt, die nachdem sie von den Spelzen befreit worden waren, bei 24° C. auf feuchtem Filtrierpapier zum Keimen ausgelegt wurden. Nach zwei Tagen wurden die Keimlinge in einer Reihe in längliche Zinkkästchen (20/3/3 cm.) voll feuchter Erde eingepflanzt, ca. 12 Pflanzen in jedes Kästchen. Die Kästchen mit den Keimlingen blieben im Dunklen bei ca. 25—26° C. 36 Stunden stehen und wurden dann, gerade wenn die Spitzen der Koleoptilen über der Erde sichtbar wurden, in das Dunkelzimmer mit konstanter Temperatur gebracht, in dem die Versuche vorgenommen werden sollten. Das Ueberführen der Versuchspflanzen in das Zimmer mit konstanter Temperatur geschah in lichtdicht verschlossenen Kästen. Wenn die Koleoptilen eine Länge von wenigstens 1.5 cm. über der Erde erreicht hatten, was weitere 24 Stunden dauerte, wurden die Pflanzen zu den Versuchen verwendet.

Da schon beim Auslegen der Haferkörner zum Keimen darauf geachtet wurde, dass nur gleich grosse Körner Verwendung fanden, und da beim Einpflanzen der Keimlinge nur solche benützt wurden, die in gleicher Zeit gleich gross geworden waren, gelang es bald, gleichmässiges und regelmässig gewachsenes Pflanzenmaterial für die Versuche zu erhalten. Waren in einem der Zinkkästchen einige Pflanzen nicht ganz gerade, so wurden sie vor dem Versuch entfernt.

Die Versuche selbst wurden im Dunkelzimmer bei konstanter Temperatur (20 C.) angestellt. Die relative Feuchtigkeit des Zimmers liess sich durch ein ständig berieseltes Tuch nahezu konstant halten (60—63 %). Schwankend war nur die Feuchtigkeit der Erde in den Zinkkästchen, da diese täglich begossen werden mussten.

Die Koleoptilen wurden gereizt, indem die bepflanzen Zinkkästchen auf einem Brett befestigt wurden, das sich um bestimmte, an einer Skala abzulesende Winkel neigen liess, ähnlich dem von RUTTEN—PEKELHARING benutzten Apparat<sup>1)</sup>. Nach der Reizung wurden die Kästchen auf den HARREVELD'schen Klinostaten<sup>2)</sup> übertragen und rotierten um die horizontale Klinostatenachse. Mit der Notwendigkeit des Uebertragens der Versuchspflanzen vom Kippbrett auf den Teller des Klinostaten war jedoch eine Fehlerquelle gegeben (Erschütterung, Unmöglichkeit genauer Horizontalage des Kästchens während des Transportes) die wohl bei Verwendung grosser Neigungswinkel unberücksichtigt bleiben konnte, bei Ablenkungswinkeln von 10° und weniger jedoch sichtlich zu Ungenauigkeiten führte. Daher wurde bei solchen und zur Kontrolle auch wiederholt bei grösseren Neigungswinkeln eine andere Versuchsanordnung gewählt. Die Reizung erfolgte auf dem Teller des Klinostaten selber. Der Teller des von mir für diesen Zweck benutzten Klinostaten nach DE BOUTER<sup>3)</sup> konnte in jede Neigung zur Vertikalen gebracht und in dieser Lage befestigt werden.

<sup>1)</sup> RUTTEN—PEKELHARING: a. a. O., 255.

<sup>2)</sup> HARREVELD, PH. VAN: Ein Universalklinostat (Rec. d. trav. bot. Néerl. 9, 1912, 170).

<sup>3)</sup> WENT, F. A. F. C.: On a new clinostat after DE BOUTER (Proc. Akad. Amsterdam 25, 1922, 475).

Nach der Reizung wurde die Klinostatenachse horizontal gestellt; gleichzeitig begann die Rotation des Klinostatentellers, sodass zwischen dem Ende der Reizung und dem Beginn der Rotation weniger als eine Sekunde verstrich und Erschütterungen der Versuchspflanzen nahezu vermieden waren.

Die Reaktionszeit schwankte zwischen 30 und 35 Minuten. Als Reaktionszeit betrachtete ich die Zeit, die zwischen dem Ende der Reizezeit und dem Zeitpunkt verstrich, bei dem 50 % der überhaupt auftretenden Krümmungen eingetreten waren. Die Ablesung des Versuchsergebnisses erfolgte jedoch erst, wenn alle überhaupt eintretenden Krümmungen sichtbar waren, also nach einer längeren Zeitspanne nach Ablauf der Reizezeit als die Reaktionszeit angibt. Der Zeitpunkt der Ablesung lag ca. 40 Minuten nach Schluss der Reizung. Nach weiteren 10 Minuten (50 Minuten nach Ablauf der Reizezeit) wurden bereits einige Krümmungen wieder undeutlich.

Als Präsentationszeit wurde die Zeit betrachtet, für deren Dauer die Versuchspflanzen gereizt werden mussten, sodass 50 % der Koleoptilen sich negativ geotropisch krümmten.

Bei der Entscheidung der Frage, ob eine Koleoptile als gekrümmt oder ungekrümmt zu betrachten ist, wird es sich nicht vermeiden lassen, eine willkürliche Grenze zu wählen, die für alle Versuche gültig zu bleiben hat. Ich habe stets Koleoptilen, die keine Krümmung, wohl aber einen deutlich monosymmetrischen Vegetationspunkt hatten, als ungekrümmt notiert (Siehe hierzu auch die Abb. von gekrümmten und deformierten Wurzelspitzen der Lupine bei RISS<sup>1)</sup>).

Es wurde zunächst die Präsentationszeit für 90° Ablenkung bestimmt, die als Grundlage zur Berechnung für die anderen Neigungswinkel dienen sollte. Sie wurde aus 45 Versuchen mit insgesamt etwa 800 Versuchspflanzen ermittelt und betrug 202 Sekunden. Die von mir gefundene Präsentationszeit ist beträchtlich kürzer als die von RUTTEN—PEKELHARING<sup>2)</sup> für *Avena*-Koleoptile ermittelte (269 Sekunden bei 24° C., also für 20° C. noch länger).

Nachdem die Präsentationszeit für 90° Ablenkung gefunden war, wurde diese auch für 60°, 45° und 30° Neigung bestimmt. Es war zuerst meine Absicht, die Präsentationszeiten für diese Winkel experimentell zu finden und dann zu prüfen, ob der gefundene Wert mit dem erst dann errechneten übereinstimmte. Diese Arbeitsweise war jedoch so zeitraubend, dass ich sie nur für den Ablenkungswinkel 45° anwandte: Präsentationszeit = 285 Sekunden. Für die weiteren Winkel verfuhr ich in der Weise, dass ich prüfte, ob die nach dem Sinusgesetz errechnete Präsentationszeit sich durch das Experiment als richtig erwies. Das war der Fall; die errechneten Präsentationszeiten für:

60° 233 Sekunden

30° 403 Sekunden

<sup>1)</sup> RISS, M. M.: Ueber den Einfluss allseitig und in der Längsrichtung wirkender Schwerkraft auf Wurzeln (Jahr. f. wiss. Bot. 53, 1914, 162).

<sup>2)</sup> RUTTEN—PEKELHARING: a. a. O., 268

zeigten sich experimentell als zutreffend: Wurden *Avena*-Koleoptilen bei den verschiedenen Ablenkungswinkeln solange gereizt, als die zugehörigen Präsentationszeitenangaben, so krümmten sich 50 % der Versuchspflanzen negativ geotropisch.

Die Bestimmung der Präsentationszeit für 45° Ablenkung erfolgte in 25 Versuchen mit insgesamt 426 Versuchspflanzen. Zur Nachprüfung der errechneten Präsentationszeiten für 60° und 30° wurden je 10 Versuche angestellt mit durchschnittlich je 20 Versuchspflanzen.

Die errechnete Präsentationszeit für 10° Ablenkung (1155 Sekunden) wurde sowohl durch Versuche auf dem Kippbrett und Uebertragen der gereizten Pflanzen auf den Teller des HARREVELD'schen Klinostaten nachgeprüft als auch durch solche, die unter Vermeidung des Uebertragens auf dem Klinostaten nach DE BOUTER vorgenommen wurden. Beide Methoden ergaben befriedigende Resultate: im Durchschnitt waren 50 % der Koleoptilen gekrümmt.

Bei einer Ablenkung von 5° konnten nur noch auf dem kippbaren Teller des DE BOUTER'schen Klinostaten eindeutige Resultate erzielt werden. Die errechnete Präsentationszeit (2312 Sekunden) wurde durch 25 Versuche mit zusammen ca. 500 Pflanzen bestätigt.

Um eine Kontrolle darüber zu haben, inwieweit eine Abweichung von der Präsentationszeit Anlass zu Schwankungen des Prozentsatzes der Krümmungen gäbe, wurden Versuche angestellt, bei denen die Koleoptilen von *Avena* etwas länger oder weniger lang gereizt wurden, als die errechnete und empirisch gefundene Präsentationszeit angab. Dabei stellte sich heraus, dass bei den grossen Neigungswinkeln (Winkel gegen 90°) schon eine sehr geringe Abweichung von der Präsentationszeit einen anderen Prozentsatz von gekrümmten Koleoptilen ergab als den bei Reizung für die Dauer der Präsentationszeit beobachteten. Die errechnete Präsentationszeit für 80° Ablenkung (205 Sekunden) ergab auch wirklich 50 % Krümmungen. Wie die nebenstehende Tabelle zeigt, krümmten sich bereits weniger als

Nr.	Dat.	Zeit	Ablenk.	Reizz.	Reaktz.	Länge d. Koleoptilen	Zahl	Ge- krümmt	Un- gekr.	%
115	18.4	6 <sup>00</sup>	90°	202 Sek.	34 Min.	1,5—2,5 cm.	16	8	8	50 <sup>0</sup> / <sub>0</sub>
120	18.4	8 <sup>00</sup>	80°	202 Sek.	35 Min.	1,75—2,5 cm.	18	8	10	45 <sup>0</sup> / <sub>0</sub>
90	1.4	11 <sup>30</sup>	80°	205 Sek.	35 Min.	1,5—2,5 cm.	24	12	12	50 <sup>0</sup> / <sub>0</sub>

50 % der Koleoptilen, wenn bei 80° Neigung 3 Sekunden kürzer, als die Präsentationszeit betrug, gereizt wurde, nämlich für die Dauer der Präsentationszeit von 90° = 202 Sekunden.

Bei den Versuchen wurden bisweilen Störungen beobachtet, die zu erklären mir nicht gelungen ist. Da diesen Störungen gewisse Gesetzmässigkeiten zu Grunde liegen, scheint es angezeigt, über sie zu berichten.

An manchen Tagen war bei den *Avena*-Koleoptilen die Präsentationszeit für die verschiedenen Ablenkungswinkel eine geringere, sodass bei Reizung in der Dauer der oben angegebenen Präsentationszeiten mehr als 50 % gekrümmte Koleoptilen beobachtet wurden.

So lieferte z. B. am 20. März bei den Ablenkungswinkeln  $5^\circ$ ,  $45^\circ$ ,  $80^\circ$  die Reizung für die Dauer der Präsentationszeit 75 %, 78 %, 80 % und 70 % gekrümmte Koleoptilen. Diese Tatsache zwang mich, an allen Tagen vor Beginn der Versuche bei den verschiedenen Ablenkungswinkeln stets erst nachzuprüfen, ob bei  $90^\circ$  Ablenkung die Reizung für die Dauer der Präsentationszeit (20 Sekunden) auch wirklich 50 % gekrümmte Koleoptilen lieferte. Erst wenn das der Fall war, konnten weitere Versuche vorgenommen werden.

Auffällig ist, dass an solchen Tagen grösserer Reizempfindlichkeit eine grössere Anzahl Pflanzen als sonst aus dem zu den Versuchen zu verwendenden Material ausgeschaltet werden musste, da ihre Koleoptilen nicht ganz gerade waren. Die Ursache für die Schwankung der Reizempfindlichkeit der *Avena*-Koleoptilen habe ich nicht ermitteln können.

Von grosser Wichtigkeit ist es, für alle Versuche Koleoptilen gleicher Länge zu verwenden (1.5—2.5 cm.). Kürzere Koleoptilen sind weniger reizempfindlich. 1 cm. lange Koleoptilen gaben bei  $60^\circ$  und 233 Sekunden (= Präsentationszeit) nur 34 % Krümmungen. Auch für lange Koleoptilen verlängern sich die Präsentationszeiten, ganz abgesehen davon, dass solche Koleoptilen sich schon deshalb nicht zu den Versuchen eignen, weil sie selten so durchaus gerade sind und senkrecht stehen, wie das unbedingt notwendig ist.

Zusammenfassend komme ich zu der Feststellung, dass für die geotropische Reizung von *Avena*-Koleoptilen das Produktgesetz, da es sich auch bei kleinen Winkeln als zutreffend erwies, uneingeschränkte Gültigkeit hat. Diese Tatsache steht im Gegensatz zu der Ansicht RISS's<sup>1)</sup>, nach welcher das Sinusgesetz für diesen Fall keine Gültigkeit beanspruchen kann.

Die Reizempfindlichkeit der *Avena*-Koleoptilen ist an gewissen Tagen eine erhöhte. Sie schwankt auch mit der Länge der Koleoptilen: Kurze Koleoptilen (1 cm. und weniger) sind weniger reizempfindlich als solche von 1.5—2.5 cm. Länge.

Erst nach Abschluss des Manuskriptes ist mir die Arbeit von BREMEKAMP in den Berichten der D. botan. Gesellschaft (43, 1925, 159.) zugänglich geworden. Die von BREMEKAMP untersuchte Dorsiventralitätskrümmung der Koleoptilen kann bei meinen Versuchen keine Fehler verursacht haben, da die Keimlinge immer in der gleichen Richtung in die Zinkkästchen gepflanzt wurden, und zwar so, dass die Längsachse der keimenden Haferfrüchte parallel zu den schmalen Wänden des Kästchens zu liegen kam. Falls Dorsiventralitätskrümmungen auftraten, so mussten diese demnach in einer Ebene erfolgen, die senkrecht stand zu der Ebene, in der die von

<sup>1)</sup> RISS; a. a. O., 208.

mir zu beobachtenden Krümmungen lagen, und können so bei der Ablesung des Versuchsergebnisses nicht zu Irrtümern Anlass gegeben haben.

Zum Schlusse möchte ich Herrn Professor WENT, der die Anregung zu der hier beschriebenen Untersuchung gab, es ermöglichte, sie an seinem Laboratorium auszuführen, und mir zu diesem Zwecke alle Hilfsmittel seines Institutes zur Verfügung stellte, ebenso sehr hierfür danken wie für das stete Interesse, das er meinen Versuchen entgegenbrachte.

*Giessen, im Mai 1925.*

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**Anatomy.** — “*The myelencephalic gland of Polyodon, Acipenser and Amia*”. By Dr. C. J. VAN DER HORST. (Central Institute of Brain Research, Amsterdam). (Communicated by Dr. C. U. ARIENS KAPPERS.)

(Communicated at the meeting of April 25, 1925).

When dissecting the brain of *Polyodon* I found a darkly pigmented, lozengeshapecd mass surrounding the foremost part of the spinal cord closely

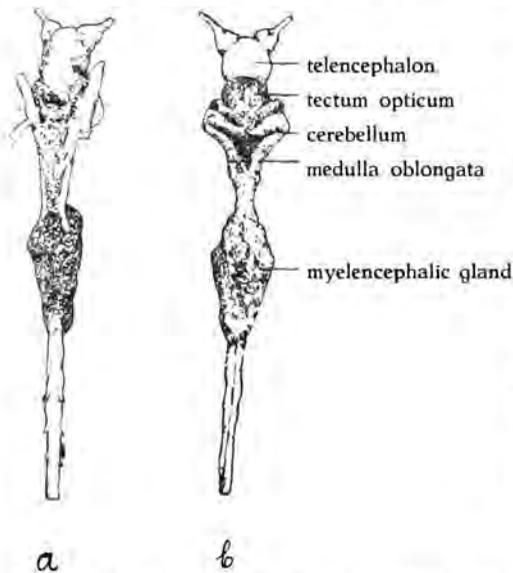


Fig. 1. Brain and frontal part of the spinal cord of *Polyodon*. *a* ventral, *b* dorsal.

behind the calamus scriptorius. This structure encircles the spinal cord very closely. At the dorsal side it reaches somewhat further caudad than at the ventral side. I prepared this mass with the brain out of the skull and have cut it in serial sections which are stained in different ways. While examining this mass, it appeared to be a bloodgland, the histological structure of which will be discussed closer in this paper.

In literature a similar gland is only known in *Lepidosteus*, where it has been accurately described and figured by CHANDLER. In this fish the

gland covers a part of the medulla oblongata, being situated a little more frontally than in *Polyodon*. CHANDLER calls it “myelencephalic gland”, a name which I wish to obtain here, though the gland is situated quite behind the myelencephalon in *Polyodon*. As this gland immediately strikes us while dissecting the brain, this somewhat more caudal situation can not be the reason that CHANDLER did not find it in *Polyodon*, no more than in *Amia*, where it is also very large and even situated on the myelencephalon, and in *Acipenser*, where the gland is to be found partly in front of and partly behind the calamus scriptorius. CHANDLER himself admits the possibility that the gland was removed together with the perimeningial tissue in the brains of the fishes, examined by him. This must have been indeed the case. In *Polypterus*, however, I could not find the gland though it certainly should still be present in the specimen dissected by me, if it had been there.

Neither could I find it in *Megalops* or in other teleosts. CHANDLER suggests the possibility, but not the probability, that the saccus endolymphaticus which covers the fourth ventricle in *Protopterus* according to BURCKHARDT may be related in some way to the bloodgland of *Lepidosteus*. Besides that here this is a real saccus endolymphaticus, so a part of the internal ear, this organ of *Protopterus* has quite a different microscopical structure than the myelencephalic gland of *Lepidosteus*, so that in my opinion all relation must be excluded. So this gland is found as a well defined structure only in *Lepidosteus* and *Amia*, *Polyodon* and *Acipenser*.

MOODIE described fossil fish brains from the coal measures of Kansas. In all probability these are brains of representatives of the Palaeoniscidae, a family related to the recent sturgeons. In these brains closely behind the calamus scriptorius a large eminence is found. MOODIE supposes this eminence to be an unpaired vagal lobe. But as such large vagal lobes are found only in Cyprinidae and Siluridae among recent fishes and not at all in Chondrostei, I think it very probable that this structure is also a myelencephalic gland.

In *Amia* the myelencephalic gland has the shape of a triangular mass

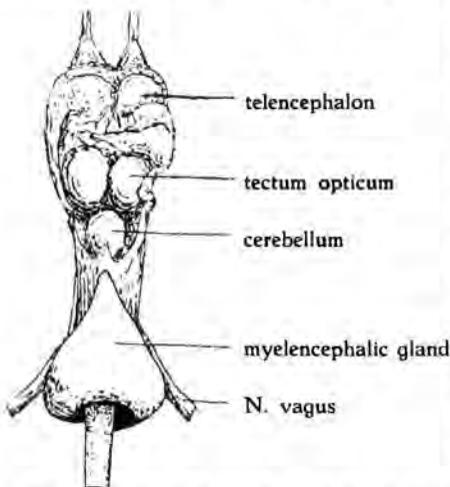


Fig. 2. Brain with myelencephalic gland of *Amia*.

that covers the fourth ventricle and the foremost part of the spinal cord. The apex of this triangle is turned to the front and reaches the caudal side of the cerebellum. At the base of the triangle the gland surrounds the spinal cord in a wide curve. According to my opinion the wideness of this curve cannot only be ascribed to shrinkage. There must be a good distance between the glandular tissue and the spinal cord in *Amia*, which is not the case in *Polyodon* and *Acipenser*. Behind the vagal root the gland is connected with a mass in the shape of a long quadrangle that reaches at the ventral side as

far frontal as is the case with the gland at the dorsal side. The earlike lobes, described by CHANDLER in *Lepidosteus*, are lacking in *Amia* as well as in *Polyodon* and *Acipenser*.

In a young specimen of *Acipenser ruthenus* I found the myelencephalic gland near the calamus scriptorius. When seen from the dorsal side it has the same shape as the gland in *Polyodon*, but at the ventral side of the spinal cord the glandular tissue is not present, so that the gland is crescentic in cross section. In a very large specimen of *Acipenser sturio* a large mass of fat is found at the same place. So it is probable that the gland in *Acipenser* degenerates in older animals. This is certainly not the case in

*Amia*, because the specimens, examined by me, were adult ones. Of *Polyodon* I possessed only young specimens of about 20 to 25 cm. total length. So I can not find out, if the gland in *Polyodon* also becomes degenerated at higher age.

At the microscopical examination the gland appears to be situated in the perimeningial tissue wholly external to the *meninx primitiva*. Whereas in *Amia* there is a great space between the *meninx primitiva* and the glandular tissue, in *Polyodon* the gland immediately touches the *meninx* and in cross section it extends from the *meninx* to the *perichondrium* (fig. 6).

The microscopical structure of the myelencephalic gland is very much like that of the spleen. The glandular tissue itself consists of rather large polygonal cells. They have a large nucleus which may be simply round, but in general it is oval or of an irregular shape (fig. 3). Often it is curved, sometimes S-shaped, sometimes the nucleus may consist of some pieces, which, nearly without mutual connection, lie scattered in the protoplasm.

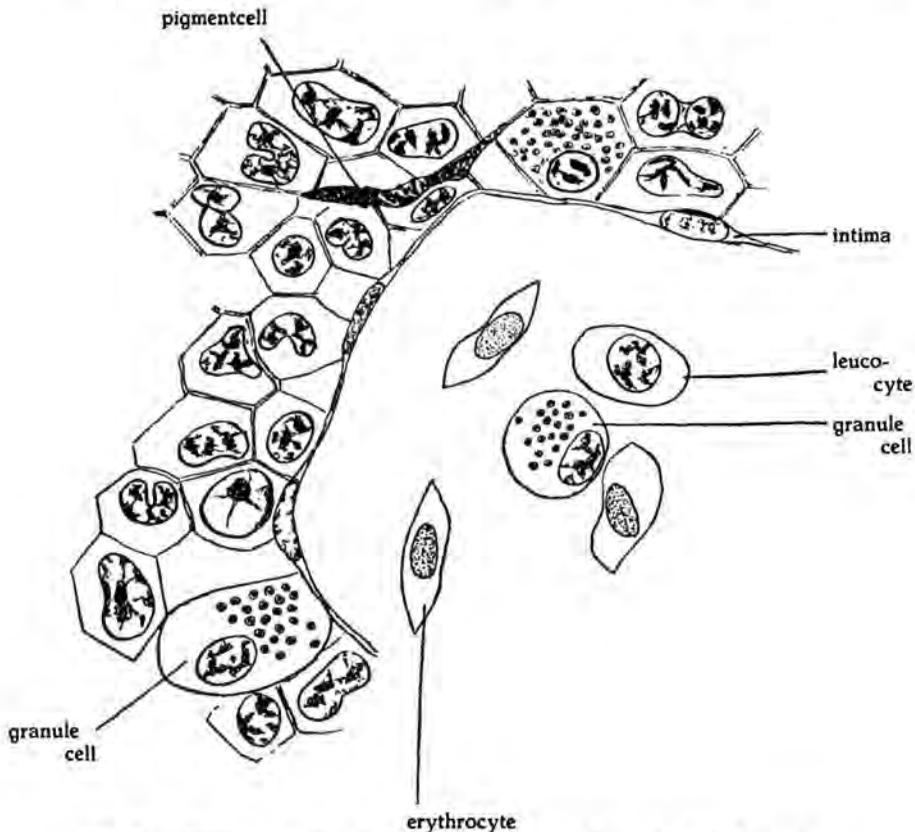


Fig. 3. Tissue and bloodsinus of the myelencephalic gland of *Polyodon*.

In this respect, as also in size, reaction to dyes and structure of the protoplasm and the nucleus these cells quite agree with the leucocytes, which are found numerously in the bloodvessels. I think I have the right

to suppose that these cells are young leucocytes which find their origin here, though I did not find mitoses. But often these cells can be seen projecting partly in a vessel.

In this tissue, cells are scattered with a more regular nucleus, which strike us by a great number of granules in the protoplasma. Some are not or hardly larger than the leucocytes, but most of them are up to twice as large. These same cells are found in certainly the same if not in greater number in the bloodvessels, also I found some projecting partly in a vessel. The number of granules in these cells varies very much. In general the small ones have few granules, the larger ones possess more, some are wholly filled with granules. These granules are strongly stained with haematoxyline, so that contraststaining with eosine had no result. Especially in Weigert-preparations these cells are very obvious, the granules being stained intensely black by this method. My material does not allow me to examine, whether we have before us oxyphil or eosinophil leucocytes with coarse granules or basiphil mastcells. According to CHANDLER the granular cells are intensively stained with eosine, KAPPERS found them stained with picrid acid. On the other hand SUNDWALL mentions that the granular cells occurring in other animals in similar places which will be discussed later on show a decided affinity to basic dyes.

According to Miss SABIN, who described the development of the different bloodcells in the chicken, the granulocytes have no relation whatsoever to the endothelial cells. Also Miss DANTSCHAROFF has demonstrated that the granulocytes are extravascular from origin. I found this confirmed in *Polyodon*. All endothelial cells have a much smaller nucleus than the leucocytes or the granulocytes. But these two latter ones are closely related to each other. As has already been said before, the granulocytes with few granules are not larger than the leucocytes and the presence or the lacking of these few granules in that case is the only difference between these cells.

In this tissue a venous network of capillaries and sinusses is found, almost quite filled with erythrocytes. These erythrocytes are oval in shape, like in all lower vertebrates, and seen from the side they are spindle-shaped, showing often a slight depression in the centre (fig. 3). They have a rather small oval nucleus, in which the chromatine is regularly distributed. In this respect they can be distinguished at once from the leucocytes, in which the chromatine is irregularly distributed. According to CHANDLER the erythrocytes are scattered freely throughout the gland, entirely independent of vessels of any sort. I could not find this in my preparations, the erythrocytes being found only in the bloodvessels. Also I think it probable that the cells, called erythrocytes by CHANDLER, are not erythrocytes, as they quite deviate from the characteristic form of these cells in other animals.

The bloodsinusses are only bordered by a well defined intima, consisting of very flat endothelial cells with oval nuclei, so they have quite the character of perimeningial bloodsinusses. In the larger sinusses the intima is continuous (fig. 3). But in the smaller ones interruptions seem to occur

in the intima. This is certainly the case, where leucocytes or granulocytes protrude in the vessels.

At the periphery the gland is more compact and the capillaries cross it in all directions, but they are few in number compared with the amount of glandular tissue. In the midst of the gland and at the dorsal side of the spinal cord, however, the number of capillaries is much more numerous. Also these capillaries run in fronto-caudal direction for the greater part. The glandular tissue between them is reduced to columns with a breadth of a few cells.

At the caudal side and dorsal to the spinal cord the glandular tissue passes in a tissue which seems to be adipose tissue. At least in the celloidine sections this tissue proves to consist of a great number of round cavities with protoplasm and some nuclei between them; cellmembranes could not be discerned here (fig. 4). This same tissue was found also at the frontal side of the gland, but here ventrally to the spinal cord. In paraffine sections this tissue is greatly deformed and looks like a reticular mass. CHANDLER

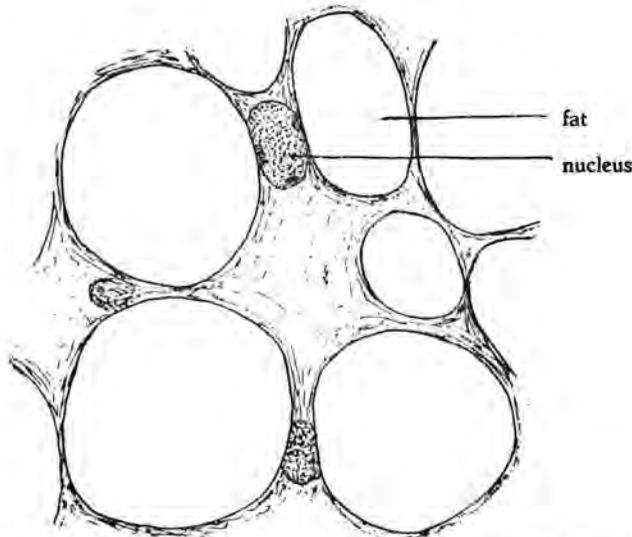


Fig. 4. Adipose tissue near the myelencephalic gland of *Polyodon*.

describes it as such in *Lepidosteus*. However, with this difference that the reticular network is found here scattered everywhere between the glandular tissue, so that CHANDLER supposes it to be a framework for the entire structure. In this tissue the bloodvessels of the gland collect in some sinusses, which are situated, for the greater part at least, frontally at the ventral and caudally at the dorsal side of the spinal cord.

In *Amia* the triangular structure covering the oblongata also consists of similar glandular tissue. As has been said before, in this animal the gland is connected behind the vagus root with a mass of tissue, situated at the ventral side of the oblongata. In the parts connecting the dorsal and ventral

masses the glandular tissue is substituted gradually by the reticular connective tissue. Probably this is also of an adipose character, though I can not say this with certainty. This tissue is very obvious in *Amia* by the great number of veins, so that the whole mass ventral of the oblongata has a somewhat red color. The dorsal side of the gland itself in *Amia* is covered also by a thin layer of the reticular tissue, whereas in *Polyodon* the glandular tissue is in direct contact with the perichondrium of the vertebral canal.

A very striking element of the gland and of the surrounding tissue are large, profusely branched pigmentcells. In *Polyodon* they are especially striking, the gland being nearly wholly black. In *Amia* I found less of these cells and they are much smaller than the pigmentcells in the membranes that cover the midbrain and the cerebellum. According to CHANDLER these pigmentcells send their branches freely in all directions between the glandu-

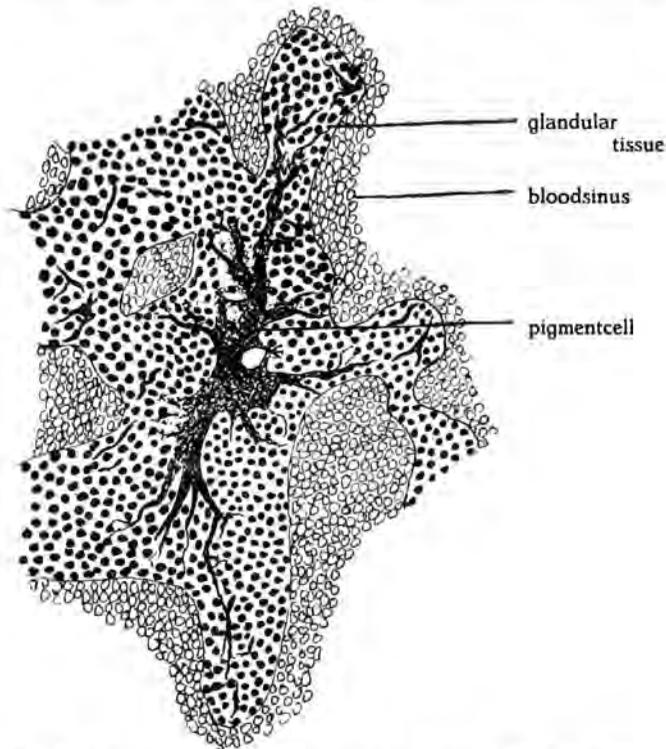


Fig. 5. Pigmentcell in the myelencephalic gland of *Polyodon*.

lar tissue in *Lepidosteus*. In *Polyodon*, however, I found these black pigmentcells in a dense layer immediately below the surface of the gland, where they arborize principally parallel to the surface, so that in cross sections they look like lines and are seen only in their real shape in the first sections that touch the gland, there where the surface of the gland is almost in the plane of the sections (fig. 5). Between the glandular tissue only a few of these cells are situated and these are scattered and send their

branches in all directions. However, they increase in number again around the spinal cord, where they arborize again parallel the surface of the spinal cord. In the connective tissue frontal and caudal to the gland only few of these pigment cells are situated except at the surface of the large bloodsinuses in this tissue, where there are many.

Concerning the bloodsupply of the gland I observed the following in *Polyodon*: Where the carotis interna reaches the brain near the infundibulum, it sends a large branch in caudal direction, the arteria encephalica posterior, described by STERZI in selachians. The right and the left artery run together in the perimeningeal tissue at the ventral side of the midbrain and the medulla oblongata in caudal direction, giving off again and again larger or smaller branches which penetrate into the brain substance. In the most caudal part of the oblongata I twice found an anastomosis of the right and the left artery; a total union to an arteria basilaris, however, as has been described by STERZI in selachians, does not exist here. But taking in account the more caudal relations, the right artery may be compared with the arteria basilaris. Later on the left artery splits up in two branches. One branch runs along the left to the dorsal side of the spinal cord and seems to serve principally for the bloodsupply of the spinal cord. The other branch curves in ventral direction and runs there caudad at a great distance from the spinal cord but still situated in the perimeningeal tissue. In the frontal part of the gland this artery approaches the spinal cord again, but here it is much smaller, so in this way it is not excluded that small sidebranches have been given off, though I could not find them. I will go on to call this artery the left one, just as the other the right one, though these names are suitable only in respect to the situation of the arteries in front of the gland. In the gland itself these names are not properly suitable, as we will see. In the mean time also the right artery has given off a sidebranch that runs along the right side of the spinal cord in dorsal direction, while the right artery itself goes on in caudal direction. Soon it splits in two equal parts, one of which runs approximately straightly caudad, while the other part curves in ventral direction but soon approaches again the spinal cord, where both parts of the right artery continue in caudal direction symmetrically situated, in the same way as happens with the right and the left artery below the medulla oblongata. In this respect the right artery corresponds to the arteria basilaris of selachians that splits also in two vessels running parallel to each other. In the foremost part of the gland these two arteries approach the spinal cord more and more, so that finally they are taken up in the meninx primitiva, which is much thickened here at the ventral side (fig. 6). In this thickened part of the meninx also the left artery penetrates running here in caudal direction between the two other arteries. The two parts of the right artery remain in the meninx primitiva and seem to serve mainly for the bloodsupply of that part of the spinal cord, that is surrounded by the gland. Gradually they diminish in size and at the caudal end of the gland they have almost disappeared. The

left artery leaves the meninx primitiva again and arborizes in the gland in a rather regular way. The small arterial capillaries fall into the much wider sinusses. With regard to the veins in relation with this gland, none of my series is in such a condition that all details could be observed completely. At the caudal end of the gland a number of sinusses and vessels is situated in the reticular tissue, surrounding the spinal cord. More caudad these sinusses decrease in size and at the end of my series they have almost quite disappeared.

It was very evident that the blood is gathered from the gland in two veins situated at both sides of the gland immediately against its periphery. In the best series, in which the brain with the gland is prepared out of the cartilaginous skull and vertebrae this lateral vein is thickest in about the

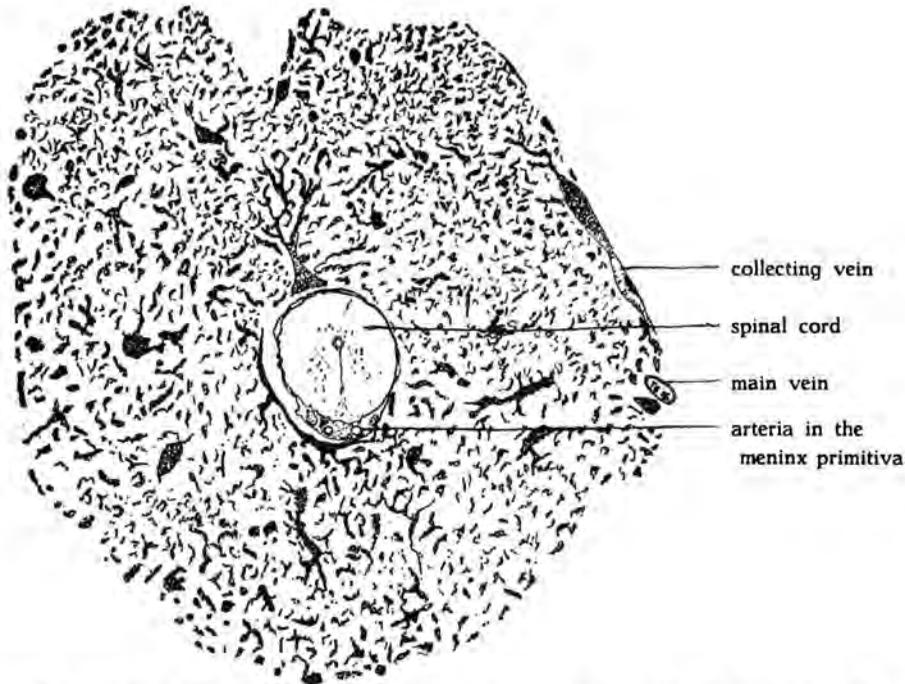


Fig. 6. Cross section showing the cervical cord surrounded by the myelencephalic gland of *Polyodon*. Only the bloodcavities of the gland are figured.

midst of the gland, also it has here a well developed wall. From this place the vein spreads as well in frontal as in caudal direction over the surface of the gland. The vein is cut off at place where it curves away from the gland in lateral direction, so I suppose that it leaves the vertebral canal here (fig. 6).

In another series a sheath of cartilage is left around the gland, but by the difference in contraction of the cartilage and the glandular tissue the sections are very much folded, some are even torn, so this series in general is less useful. However, I found here a vein leaving the vertebral canal

together with a spinal nerve. At the frontal side a vessel strikes us, running at the dorsal side of the spinal cord from the gland to the choroid plexus of the fourth ventricle and splitting up in a number of sinusses lying on this membrane (see also fig. 6). This vessel can be distinguished immediately from the other sinusses and veins by the great number of pigment cells lying along the thin wall in the same way as is the case in arteries.

Against the wall of other venous bloodvessels also pigment cells are found but in far smaller number.

Furthermore frontal of the gland and at the ventral side of the spinal cord a great number of venous cavities is found, which anastomose again and again. A little caudal of the *calamus scriptorius* a part of this cavities curves around the spinal cord in order to spread on the choroidal roof of the fourth ventricle.

Most of the blood, however, seems to flow away through a wide vein, that leaves the perimeningial tissue in the ventral midline.

It still remains an open question whether the blood runs from the gland to the choroidal roof through the dorso-median vein or in the opposite direction from the choroid to the gland. The latter seems more probable to me. In the first place because an artery comes from the midbrain in the dorsomedian line that arborises in the choroidal plexus and secondly both *venae encephalicae posteriores*, that run, according to STERZI, parallel the *vagus* and discharge the blood from the plexus in Selachians are lacking here.

As said before I found this myelencephalic gland only in *Polyodon*, *Acipenser* and *Amia*, while it has been described also by CHANDLER in *Lepidosteus*, which is confirmed by KAPPERS.

In other fishes, Cyclostomes, Selachians, Teleosts, *Polypterus*, which I have studied, I found no gland. However, this does not prove that there is really nothing at all. As one of the components of the gland I have described the very characteristic granular cells. I found — like KAPPERS — the same granular cells in great numbers in *Ceratodus*, scattered on the choroid plexus of the fourth ventricle between the numerous bloodvessels and in the meningial tissue. Indeed these granular cells seem to occur in vertebrates in general. So SUNDWALL has described them accurately in different mammals, they are mentioned also by DEWEY. GOLDMANN described them in rats as pyrrolcells. It is difficult to say in how far the mastcells, described by MCKIBBEN in *Necturus*, as also the "Wanderzellen" mentioned by KOLMER, correspond to the granulecells, as I found in *Polyodon*.

As said by MCKIBBEN, the mastcells in the meninges of *Necturus*, if studied superficially look like neurones on account of their long thin branches. Also the "Wanderzellen" figured by KOLMER in *Triton* have the same shape. It is remarkable that these cells occur also at the ventricular side of the choroid membrane. Although I do not doubt KOLMER's statement, I have never seen this in the preparations of the different amphibians, which I studied. According to KOLMER these cells occur in the

choroid plexus of all vertebrates, so in the same place, where SUNDWALL and other authors found the more simply shaped granulecells. So it seems probable to me that we are dealing here with the same cells and that the difference in shape is only the result of the functional state and perhaps of the fixation. LEHNER also has shown that mastcells may make amoeboid movements and lately NEUMANN mentioned that also the eosinophil cells are able to do so.

I did not find the granule cells that occur in such a large number in the myelencephalic gland in the choroid of the fourth ventricle in *Polyodon*. This indicates that these cells, scattered in other vertebrates, are accumulated in a structure of definite form in these four fishes. This seems also to be the case in reptiles, but in a much less degree, at least KOLMER mentions accumulations of a typical shape on the choroid plexus near the *calamus scriptorius*.

Different authors have indicated (KAPPERS, KOLMER, a.o.) that the plexus can be vascularised to such an extent that it can be looked upon as a bloodgland. So KOLMER found all lymphatic elements in it in a great number especially in the dog and says that it gives the same impression as small pieces of bone marrow scattered on the choroid.

In the four mentioned ganoids we do not only find a localisation but also an enormous increase of the granule cells compared with other vertebrates. And furthermore the organ has the typical structure of a bloodgland.

There are different opinions about the function of the granule cells. Some authors suppose the granules to be nucleines, others derivatives of haemaglobine and the opinion exists also that the granules contain oxydases. I think that the granule cells are of phagocytic character. In the blood-cavities of the myelencephalic gland I found many more or less deformed erythrocytes and these were always in the neighbourhood of the granule cells. Also the granules are always stained in the same way as the nuclei of the erythrocytes. This was striking especially in the Weigert preparations, where only these granules and nuclei are intensively black, whereas the nuclei of the other cells are red by the contraststaining with paracarmin.

For an experimental research of the function of the granule cells, especially in relation to their situation on the choroid or in the neighbourhood of the brain, the fishes, mentioned in this article, are a very good material, because here the whole organ and together with this all granule cells can be removed easily, whereas in other vertebrates this is excluded on account of their widely spread occurrence.

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**Geology.** — "*Concerning the Existence of Elevation Craters in the Dutch East Indies, as supposed by some geologists.*" By L. RUTTEN.

(Communicated at the meeting of February 28, 1925).

It is well-known that in the controversy between the adherents to the Accumulation-theory (SCROPE) and the Elevation-theory of craters (VON BUCH) F. JUNGHUHN<sup>1)</sup> has sided with SCROPE, in the light of his own experience of volcanoes in Java. We also know that the accumulation-theory was paramount during many decennia, but that gradually a greater activity was again assigned to the magma. It has been conclusively demonstrated that the magma is possessed of such intrinsic energy, that under certain circumstances it can force its way through the earth's crust even there where no fissures existed before. Some authors, however, went the length of assigning an elevating power to the magma, and again accepted VON BUCH's theory of the existence of "Elevation-Craters". Strange to say, in the same Dutch Indies, which had formerly furnished so many arguments for the accumulation-theory, geologists now supposed to discover instances of Elevation-Craters.<sup>2)</sup> One of these instances has even found its way in a great Textbook of Geology<sup>3)</sup>.

It is not my object to ascertain whether real Elevation-Craters have been found in other regions. My intention is only to show that the instances adduced from the archipelago do not afford any evidence whatever in favour of "Elevation-Craters". I feel the more prompted to do so as, to my knowledge, the views of VOLZ and RECK (l.c.) have never been contradicted, while moreover VOLZ's conception has been more or less authorized by KAYSER in his Textbook.

W. VOLZ holds that the porphyrites, which according to him and to J. HOOZE<sup>4)</sup> constitute the nucleus of the northern part of Pulo Laut, to the east of Borneo, are younger than the surrounding sediments, and that the porphyritic magma in forcing itself upwards has raised the latter so as to form a dome. To maintain this view he had in the first place to alter HOOZE'S representations of the geology of the island, since according to HOOZE (l.c.) in the island of P. Laut an eocene formation of sandstones,

<sup>1)</sup> F. JUNGHUHN, Java, 1854. III.

<sup>2)</sup> W. VOLZ, Neues Jahrb. f. Mineralogie etc. Beil. Bd. XX. 1905. p. 354—364.

H. RECK, Zeitschr. d. Deutsch. geol. Ges. 1910. Monatsber. p. 292—318.

<sup>3)</sup> E. KAYSER, Lehrb. der Geologie, II. 6e ed. 1921, p. 6.: „In gleicher Weise hat W. VOLZ auf der Insel Pulo Laut bei Borneo einen Fall von Aufbiegung der Schichten in Folge eines grossen Magma-Ergusses beobachtet“.

<sup>4)</sup> J. A. HOOZE, Jaarb. Mijnw. 1888. Techn. Adm. Gedeelte, p. 337—429.

shales, and pitchcoal of about 100 m. thickness superimposes older porphyrite and diabase, while farther southward, in the centre of the island, HOOZE also recognizes diorite and serpentine. VOLZ, on the other hand, maintains that the porphyrites in the north are posteoocene. True, HOOZE has not produced cogent evidence for the asserted older age of the porphyrites. This assertion is quite conceivable, however, when we reflect that in HOOZE'S time it was universally accepted that a formation, consisting of porphyrites and diabases, and to which also diorite and serpentine are added, must needs be pretertiary. The only passage in HOOZE'S work that may be called evidential, is found on p. 406: „where the diabase is in contact with the tertiary coal-formation, we are often confronted with a conglomerate-, and breccia-formation (Pamantjangan. Selaru etc.), which, therefore, is usually to be considered as the basis of this coal-formation". VOLZ has justly remarked, that these conglomerates and these breccia of volcanic material might as well be contact breccia (l.c. p. 360). It must be admitted, therefore, that HOOZE has not proved conclusively that the tertiary deposits are younger than the igneous rocks. But neither has the reverse been proved by VOLZ, in spite of his three arguments in favour of the higher antiquity of the sediments (l.c. p. 359).

In the first place he found "im Urwald einen Contact von Porphyrit und Thon; der Thon war direct am Contact auf geringe Entfernungen gefrittet". Now it is certain that for a contact between a very thick diabase- and a porphyrite-mass of 5 km. broad, this contact-metamorphism must be considered very poor. Further contact-metamorphism is absolutely unknown: the composition of the coal is invariably that of the normal Borneo eocene coal; the pelitic rocks possess the normal consistency of old tertiary shales; the sandstones display no trace of contact metamorphism and the Foraminifera-limes and the Orbitoides previously examined by the present writer had changed only very little diagenetically<sup>1)</sup>. However, every one, acquainted with disclosures in primeval forests, knows how little a supposed contact between porphyrite and burnt clay signifies. In a primeval forest with intense, partly lateritic weathering, many things can gradually assume the appearance of burnt clay. Indeed, VOLZ himself seems not to attach great value to this argument.

In the second place volcanic tuffs near Sigam are lying rather level, while in the vicinity eocene layers show dips of 18°—30°; lastly, and this is considered by VOLZ to be the most important argument — in the valley of the Sg. Semblimbingam horizontal tuffs occur between upheaved eocene layers in the west, and porphyrite in the east. It stands to reason — as also appears from VOLZ'S picture — that we have not to do here with a continuous row of disclosures. It now seems to me that these observations cannot prove anything, since VOLZ has not shown that the deposits, supposed to be tuffs, are not detritus of older volcanic

<sup>1)</sup> L. RUTTEN, Jaarb. Mijnw. 1914. Verh. 2. 1915. p. 74—77.

rocks which have been very recently redeposited. This possibility deserves no doubt consideration because deposits in a valley are concerned. It may be difficult to demonstrate this, but unless this proof be brought forward the youth of the porphyrites cannot be considered as established.

So, for the present the age of the P. Laut porphyrites remains doubtful, although there seem to be indications of their being younger than eocene. But we know that there are many difficulties in establishing the age of effusive rocks in the tropics, notably in South Borneo. The literature confirms this. The effusive rocks in the neighbourhood of Pengaron were supposed by VERBEEK to be decidedly posteocene<sup>1)</sup>; HOOZE considered them as cretaceous porphyrites<sup>2)</sup> while Kemmerling again referred them to the posteocene, with some reserve, though<sup>3)</sup>.

In addition I wish to say that a sandstone from Kota Baru in P. Laut, (near the lighthouse) collected by myself some ten years ago, has been entirely (or nearly so) made up of quartz-grains and finely granular siliceous rocks, while also HOOZE (l. c. p. 376) records that the sandstones from the eocene of P. Laut are often of a pure white. This would not imply a higher age of the porphyrites, inasmuch as in the sandstones the detritus of the porphyrites is lacking altogether. There is, however, a possibility that this detritus occurs only in the lowermost parts of the eocene formation.

In the second place VOLZ has failed to show that the entire nucleus of northern P. Laut is composed of diabases and porphyrite, that we have really to do here with an extensive, connected eruptive mass. With the exception of his discovery of diabase-porphyrine at the highest top of the island, HOOZE's observations have been restricted to the coastal zone. VOLZ, it is true, has traversed the whole island ("Das Gebirge ist mit dichtem Urwalde bedeckt" p. 356), but there is no evidence whatever of his having then gathered enough geological data to warrant the conclusion that the entire nucleus of northern P. Laut is one continuous eruptive mass. Given the fact that in the south of this island quartz-diorite and serpentine occur, which elsewhere in S. Borneo are often associated with schists, I do not think it at all impossible that these rocks occur also in the centre of the northern part of the island, and that the material of the sandstones from the eocene has been supplied by the schists. It would probably put any engineer in P. Laut to very little trouble if he should devote his off-days to some excursions in the principal valleys on the west coast, in which the very boulders would supply important hints as to the structure of the rocks in the interior.

So, when propounding his highly important hypothesis: "Die Insel Pulo Laut... (ein) Beispiel einer Hebung durch einen Massenerguss".

1) R. D. M. VERBEEK, Jaarb. Mijnw. 1875, I. p. 3-130.

2) J. A. HOOZE, Jaarb. Mijnw. 1893, p. 1-431.

3) G. KEMMERLING, Tijdschr. Kon. Ned. Aandr. Gen. 1915. p. 717-774.

VOLZ has omitted to prove two very weighty matters: 1<sup>o</sup> that the eruptiva are indeed posteocene; 2<sup>o</sup>. that the nucleus of P. Laut is indeed one large continuous mass of eruptiva <sup>1</sup>).

But even if future investigation should put VOLZ in the right on these two points, Pulu Laut would never afford *conclusive evidence* for the existence of Elevation-Craters or of related phenomena. It may reasonably be *believed* that the eruptiva of P. Laut have pushed up a portion of the earth's crust, but every effort to prove this would be hampered by the fact that P. Laut lies in the region of S.-E. and E. Borneo, where folding is a normal phenomenon, and where the main trend of the folding movements coincides with the direction of the eocene strata in the island, so that it might always be argued that the upheaval of the strata results from normal folding <sup>2</sup>), which would, indeed be the most plausible view. VOLZ slurs over this difficulty when he says: "Zwar wurde Indonesien nach dem Eozän so wie an der Wende von Tertiär und Dilivium von Faltungen heimgesucht (deren Wesen und Wirkung aber für Borneo so gut wie unbekannt ist), aber ich glaube nicht, dass man die oben beschriebenen, eigenartigen aber geringfügigen Dislokationen auf eine Faltung zurückführen kann" (p. 363). Now, VOLZ could have known that as early as 1905 records were on hand, from which various information regarding the folding in Borneo could be obtained. Not only had C. SCHMIDT <sup>3</sup>) pointed out, in accordance with modern conceptions, that there are in N. W. Borneo normal, tertiary folding-mountains, but since long folding processes in the tertiary had also been established for S. Borneo and E. Borneo <sup>4</sup>). It might still be assumed that in some localities those folding processes were owing to the action of igneous rocks — a conception which, from its very nature, may occasionally be met with in the oldest literature — but in many other localities no facts could be discovered that implied the co-operation of igneous rocks in the folding process. In some places the folds were very sharp, in others weak, while the anticlines displayed the semi-domelike shape, which is known from P. Laut (i. a. at the Berau-river. HOOZE l. c.). Besides in VOLZ'S time already the literature contained records concerning the general tectonic trend in S. E. and E. Borneo N.-E. to N.-N.-E., which consorts with the main trend of the coal-layers

<sup>1</sup>) While I was correcting the proofsheets E. GÖLLNER'S publication (Jaarb. v. h. Mijnw. 50, Verh. 1, 1921, 1924) came to my notice. It seems to show that VOLZ'S view is erroneous, and that porphyrites and the diabases of P. Laut are pre-eocene.

<sup>2</sup>) It should be noted that the interpretations given by HOOZE of the causes of the upheaval of the eocene strata in P. Laut are very primitive, and slightly contradictory inter se: VOLZ refers to these conceptions at large — which, by the way, were completely out-of-date even in his time.

<sup>3</sup>) C. SCHMIDT, Bull. Soc. géol. de France (IV). 1. 1901. p. 266—267.

<sup>4</sup>) See also for S.-E. Borneo VERBEEK l. c. 1875, HOOZE l. c. 1893; for Kutei HOOZE Jaarb. Mijnw. 1887 Tech. Adm. Ged. and 1888 Techn. Adm. Gedeelte; for Berau HOOZE Jaarb. Mijnw. 1886 Tech. Adm. Ged.

in P. Laut. These data have of course been largely accentuated by subsequent researches<sup>1)</sup>, so that we feel sure nowadays that a perfectly normal tertiary range of folding mountains runs all along the east coast of Borneo, certainly as far as the Dutch boundary in the north.

Consequently VOLZ'S pronouncement that P. Laut is an instance of upheaval through volcanic eruption is unproved, unprovable and contrary to all reasonable expectation.

H. RECK (l.c.) thought he could point out several Elevation-Craters in Java, but in doing so he committed even more serious errors than VOLZ. In the first place he refers to the G. Lima to the east of Patjitan: In the middle of VERBEEK and FENNEMA'S map<sup>2)</sup> there occurs a diatrema: "zwischen ihm und das jüngere Miocän schiebt sich ein Kranz älteren Miocäns, das den Kern von allen Seiten umschliesst, ein Lagerungsverhältniss, das nur durch die vulkanische emportreibende Kraft des zentralen Kernes erklärt werden kann" (p. 308). Obviously RECK has neglected to study properly the text accompanying VERBEEK and FENNEMA'S map, else he would have seen, that the nucleus of the G. Patjitan is referred to the "old Andesites", that the inner rim of miocene belongs to the  $m^1$ , and is, therefore, younger than the nucleus, and that the outer rim of  $m^3$  is of course still younger; consequently it is clear that according to VERBEEK and FENNEMA the older andesite can never have pushed up the younger miocene ( $m^1$  and  $m^3$ ). It is very well possible, though, that the true condition differs from the one illustrated on the map, but even then the existence of "Elevation-Craters" cannot reasonably be assumed. At all events for the present the G. Lima near Patjitan does not furnish any evidence *in favour* of the Elevation-Crater theory. Furthermore RECK has endeavoured to prove that the G. Butak in North-Rembang is a typical Elevation-Crater (because the tertiary strata dip away radially from the mountain) and that the present elevated position of the tertiary mass between G. Putjak and Lasem (Ngargopuro) resulted from a volcanic upheaval, "da eine so starke tektonische Aufwölbung in dieser Gegend gänzlich überraschend wäre" (p. 310).

Here again RECK has disregarded without bringing forward fresh evidence VERBEEK and FENNEMA'S view that the three andesite-massifs belong to the "old andesites" and are older than the surrounding  $m^3$ . But even when admitting what came true later on<sup>3)</sup>, viz. that the volcanic masses of North Rembang are younger than most sediments surrounding them, it will not do to use RECK'S arguments in favour of Elevation-

<sup>1)</sup> See i.a. H. JEZLER, Z.f. prakt. Geologie. 1916, p. 77—85, 113—125; L. VAN ES, Jaarb. Mijnw. 1917. Verh. 2. p. 5—143; L. KROL, Jaarb. Mijnw. 1918. Verh. 1. 1920, p. 281—367.

<sup>2)</sup> R. VERBEEK et R. FENNEMA, Géologie de Java et Madoura. 1896.

<sup>3)</sup> C. 'T HOEN, Jaarb. Mijnw. 1916. Verhand. 2. p. 202—254.

Craters. Indeed, from VERBEEK and FENNEMA's map we knew already that North-Rembang is situated in a true folding region. Now it is not at all strange that when a complex of sediments including a diatrema are folded collectively, the sedimentary strata will, after the folding process, usually dip away from the more rigid eruptive masses. It might also be conceived — without assigning elevating power to the magma — that in certain cases an eruptive mass, which forces itself upwards just when the folding is taking place, goes to the highest parts of the anticlines, i. e. to their dome-shaped elevations. Neither is the fact that part of the tertiary sediments lies on a rather high topographical level, in any way indicative of volcanic upheaval, as we knew already from the profile of VERBEEK and FENNEMA that considerable amplitudes occurred during the folding of the tertiary, and also that since that folding intense denudation has taken place. The actual occurrence of tertiary masses on such a great height may be readily explained if we assume that there the tertiary has been preserved between two more resistant masses of volcanic rocks, whereas elsewhere it has, at such a level, been long since denuded.

Meantime our knowledge of the geology of the region has been greatly clarified by 'T HOEN's profiles (l.c.) so that RECK's conceptions are still less excusable. It now appears that the G. Butak andesite has pushed itself upon an anticline, but not on its highest part, because from the W. the sediments dip away under the G. Butak. It also appears, on the contrary that the G. Lasem has come to eruption above a synclinal region and that on all sides the sediments dip away under it, while lastly the G. Putjak has come to eruption at the side of an anticline. Further it appears that, besides the half-dome in which the G. Butak-andesite has broken through, two other beautifully formed domes occur in the territory (that of Ngandang-Lodan and that of G. Banju-Uja) into which, however, no andesite masses have broken through. He who is familiar with the geology of Java, also knows that further southward in Rembang there are still a number of dome-shaped elevations, on which the oil-boring territories are situated. The domes, therefore, have originated through normal orogenic movements and only once — the G. Butak — has an andesite-mass broken through.

*The conclusion, therefore, is warranted that neither the observations made by VOLZ, nor the interpretations brought forward by RECK tend to prove anything for the existence of Elevation-Craters in the Dutch East Indies.*

*Utrecht, Jan. 14, 1925.*

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**Mathematics.** — “*A Representation of the Plane Pencils in  $R_3$  on the Conics of a Plane*”. By Prof. J. WOLFF. (Communicated by Prof. JAN DE VRIES).

(Communicated at the meeting of March 28, 1925).

This paper owes its origin to a talk with Prof. JAN DE VRIES, where the latter raised the question whether such a representation can be easily brought about.

1. We assume in  $R_3$  four non-coplanar points  $A_1, A_2, A_3, A_4$ , and a plane  $\alpha$  which does not contain any of the four points  $A_i$ . The point of intersection of  $\alpha$  with the line  $A_i A_j$  we call  $B_{ij}$ , the intersection of the plane  $A_j A_k A_l = \alpha_i$  with  $\alpha$  we call  $b_i$ . Further we choose a point  $A$  in  $\alpha$  which does not lie on any line  $B_{ij} B_{kl}$  nor on any  $b_i$ .

The  $\infty^5$  quadratic surfaces through the four points  $A_i$  we call  $O^2$ . If  $(P, \pi)$  is a plane pencil ( $P$  and  $\pi$  are resp. the point and the plane of the pencil), we associate to it the  $O^2$  for which  $P$  is the pole of  $\alpha$  and  $A$  the pole of  $\pi$ .  $O^2$  cuts  $\alpha$  in a conic  $k^2$ , the image of  $(P, \pi)$ .

2. Any non-degenerate conic  $k^2$  of  $\alpha$  is the image of one plane pencil. For one  $O^2$  passes through  $k^2$ ; otherwise there would pass through it a pencil  $O^2$  of which the base curve would consist of  $k^2$  and another plane conic which would pass through  $A_i$ . Further  $\alpha$  has one pole  $P$  outside  $\alpha$  with regard to  $O^2$  because  $k^2$  is non-degenerate and for the same reason  $A$  has one polar plane  $\pi$  through  $P$ . The plane pencil  $(P, \pi)$  has  $k^2$  as image.

3. If  $k^2$  consists of two straight lines  $k$  and  $k'$  with point of intersection  $P$  outside  $\alpha$ , and if the  $O^2$  through this  $k^2$  is not a cone,  $P$  is the (only) pole of  $\alpha$  relative to  $O^2$ , and  $A$  has one polar plane  $\pi$ , (through  $P$ ), hence  $k^2$  is the image of one plane pencil  $(P, \pi)$ .

If  $O^2$  is a cone with vertex in  $\alpha$ ,  $A$  has one polar plane  $\pi$  with regard to  $O^2$  and  $\alpha$  has one polar line  $\lambda$  unless  $O^2$  consists of two planes which cut each other along a line in  $\alpha$ . Apart from the latter case  $k^2$  is the image of the  $\infty^1$  plane pencils  $(P, \pi)$  where  $P$  describes the line  $\lambda$ . There are 7  $O^2$  which each consist of two planes with intersection in  $\alpha$ , to wit 4  $O^2$  each consisting of a plane  $\alpha_i$  and the plane through  $A_i$  and the intersection  $b_i$ , besides the 3  $O^2$  of which each consists of the planes  $A_i A_j B_{kl}$  and  $A_k A_l B_{ij}$ . Now  $A$  has one polar plane  $\pi$  relative to each of the 7 pairs of planes, hence each of the 7

double lines  $b_i$  and  $B^{ij} B_{ki}$  is the image of the  $\infty^2$  pencils that fill a plane  $\pi$ . The 7 straight lines are the sides and the diagonals of a quadrilateral.

If  $k^2$  consists of 2 straight lines  $k$  and  $k'$  through  $A$  and if the  $O^2$  through this  $k^2$  is not a cone, only the pencil  $(A, a)$  is associated to  $k^2$ . If  $O^2$  is a cone  $K^2$ ,  $a$  has a polar line  $\lambda$  relative to  $K^2$ ; if  $P$  is a point on  $\lambda$  and  $\pi$  an arbitrary plane through  $P$ ,  $k^2$  is the image of the plane pencil  $(P, \pi)$ , for  $A$  is the pole of  $\pi$  and  $P$  is the pole of  $a$  relative to  $K^2$ . These singular pairs of lines  $k, k'$  form an involution, the associated  $K^2$  form the pencil of cones with vertex  $A$  (through the  $A$ ); hence the  $\lambda$  form a quadratic cone  $\Lambda^2$ .

Summarizing: *all the singular  $k^2$ , images of an infinite number of plane pencils, are degenerate. They are:*

1. *the  $\infty^3$  intersections of the cones  $O^2$  with vertices in  $a$  outside  $A$ . Apart from 7 double lines, intersections of pairs of planes, each of them is the image of  $\infty^1$  plane pencil  $(P, \pi)$  in a plane  $\pi$  where  $P$  describes a straight line. The 7 double lines, sides and diagonals of a quadrilateral, are each the image of the  $\infty^2$  pencils in a plane  $\pi$ .*

2. *The  $\infty^1$  intersections of the cones  $K^2$  with vertex  $A$ . Each is the image of the  $\infty^3$  plane pencils of which the carrier  $P$  describes a line  $\lambda$ . These  $\lambda$  form a quadratic cone  $\Lambda^2$  with vertex  $A$ .*

4. Now we shall try to find the singular plane pencils (to which an infinite number of  $k^2$  are associated). We begin with the case  $P \neq A$ .  $A$  is the pole of  $\pi$  and  $P$  is the pole of  $a$  for two  $O^2$ , hence for a pencil. This contains a cone  $K^2$  with vertex  $A$  and  $AP$  is the polar line  $\lambda$  of  $a$  relative to  $K^2$ ;  $P$  lies, therefore, on  $\Lambda^2$ . The pencil also contains a cone  $L^2$  with vertex  $P$  and  $\pi$  is the polar plane of  $\lambda = AP$  relative to  $L^2$ . The polar planes of  $\lambda$  relative to the cones  $L^2$  with vertex  $P$  form a pencil of planes through a straight line  $r_p$  through  $P$ . Hence  $\pi$  passes through  $r_p$ . If inversely  $P$  is an arbitrary point of  $\Lambda^2$  and  $\pi$  is an arbitrary plane through  $r_p$ ,  $A$  is the pole of  $\pi$  and  $P$  the pole of  $a$ , relative to a cone  $L^2$  with vertex  $P$  as well as relative to a cone  $K^2$  with vertex  $A$ ; consequently  $(P, \pi)$  has for image any individual of the pencil  $k^2$  to which the intersections of  $K^2$  and  $L^2$  with  $a$  belong.

A plane pencil  $(A, \pi)$  with  $\pi \neq a$  has as images the  $\infty^1$  pairs of lines  $k, k'$  of the involution in  $A$ . For  $A$  must be the pole of  $\pi$  and of  $a$ ; consequently  $O^2$  is a cone  $K^2$  with vertex  $A$ . The plane pencil  $(A, a)$  has all the  $\infty^2$  pairs of lines through  $A$  as images.

Summarizing: *the singular plane pencils all have their carriers  $P$  on  $\Lambda^2$ . The singular plane pencils that have an arbitrary point  $P$  of  $\Lambda^2$  as carrier, form a pencil of planes. Each of these pencils has as images the  $k^2$  of a pencil to which a pair  $k, k'$  of the involution in  $A$  belongs. A plane pencil  $(A, \pi)$  has all these pairs as images, the plane pencil  $(A, a)$  has the  $\infty^2$  pairs of lines through  $A$  as images.*

If  $P$  is a point of intersection of a line  $A_i A_j$  with  $A^2$ , the cones  $L^2$  with vertex  $P$  form a net, hence all the plane pencils with carrier  $P$  are singular; their images form the intersections with  $\alpha$  of pencils containing the  $K^2$  corresponding to  $\lambda = AP$  and the  $L^2$  of the net. Accordingly: *there are 12 sheaves of singular pencils.*

The pencil  $K^2$  contains 3 pairs of planes of which the double lines  $d_1, d_2, d_3$ , lie on  $A^2$ . If  $P$  is a point on  $d_i$ , the polar plane  $\pi$  of  $A$  relative to all  $L^2$  is a fixed plane  $\pi$ . Hence the pencil  $(P\pi)$  has as image all the  $k^2$  of the net to which belong the pencil which is the intersection of the pencil  $L^2$  with  $\alpha$ , and the pair of lines in which the pair of planes that has  $d_i$  as double line, cuts  $\alpha$ . 6 of the said 12 vertices of singular pencils lie in pairs on the lines  $d_i$ .

5. Let  $\pi$  be an arbitrary plane. The  $O^2$  corresponding to the  $\infty^2$  pencils in  $\pi$  must satisfy the condition that  $A$  is a pole of  $\pi$ . Hence the  $\infty^2$  pencils in a plane  $\pi$  are represented as the  $k^2$  of a net  $\nu(\pi)$ . As  $\pi$  cuts all the generatrices of  $A^2$ , it ensues from § 3 that  $\nu(\pi)$  contains all the intersections of  $\alpha$  with the cones  $K^2$  with vertices  $A$ . These intersections form a pencil  $\varrho_0$ .

*The  $\infty^3$  fields of pencils, each consisting of the  $\infty^2$  pencils of a plane, are represented in the  $\infty^3$  nets through the fixed pencil  $\varrho_0$ .*

§ 6. Let  $P$  be an arbitrary point. The  $O^2$  corresponding to the  $\infty^2$  plane pencils with vertex  $P$ , satisfy the condition that  $P$  is the pole of  $\alpha$ . Hence the  $\infty^2$  pencils that have  $P$  as vertex, are represented as the  $k^2$  of a net  $\nu(P)$ .

7. The  $\infty^2$  conics  $k^2$  of  $\alpha$  form a plane space  $\Sigma_5$ . Any point of  $\Sigma_5$  gives a  $k^2$ , hence also an  $O^2$  through  $A_1, A_2, A_3$  and  $A_4$ . In this way the  $\infty^5$  pencils of  $R_3$  are the images of the points of  $\Sigma_5$ . The  $\infty^2$  plane pencils of a plane  $\pi$  of  $R_3$  have as images the points of a plane  $\nu(\pi)$  of  $\Sigma_5$  passing through a fixed straight line  $\varrho_0$ . The  $\infty^2$  plane pencils with a point  $P$  as vertex are represented on  $\Sigma_5$  as the points of a plane  $\nu(P)$ .

The net  $O^2$  consisting of a plane  $\alpha_i = A_j A_k A_l$  and an arbitrary plane through  $A_i$  is represented as a plane  $\nu_i$  of  $\Sigma_5$ . Each pair of planes  $\nu_i, \nu_j$  has a point  $G_{ij}$  in common, the image of the pair of planes  $\alpha_i, \alpha_j$ . The lines  $G_{ij} G_{ik}, G_{ik} G_{il}, G_{il} G_{ij}$  in  $\nu_i$  are the images of three pencils  $O^2$  the individuals of which consist of  $\alpha_i$  and the planes through  $A_i A_l$ , resp.  $A_i A_j$ , resp.  $A_i A_k$ . Accordingly we find in  $\Sigma_5$  a configuration of 4 planes  $\nu_i$ , 12 straight lines  $G_{ij} G_{ik}$  and 6 points  $G_{ij}$ ; any plane  $\nu_i$  contains 3 points  $G_{ij}, G_{ik}, G_{il}$ ; through each point  $G_{ij}$  there pass 4 straight lines to  $G_{ik}, G_{il}, G_{jk}, G_{jl}$ ; on each straight line there lie 2 points  $G_{ij}, G_{ik}$ ; through each point  $G_{ij}$  there pass 2 planes  $\nu_i$  and  $\nu_j$ .

The  $O^2$  consisting of a plane through  $A_i A_j$  and a plane through

$A_k A_l$  are represented as the points of a quadratic surface  $\Omega_{ij} = \Omega_{kl}$  which passes through the 4 lines  $G_{ik} G_{il}$ ,  $G_{jk} G_{jl}$ ,  $G_{li} G_{lj}$ ,  $G_{ki} G_{kl}$ , which form a skew quadrilateral. Each pair  $\Omega_{ij}$ ,  $\Omega_{ik}$  has 2 points  $G_{il}$  and  $G_{jk}$  in common. The 3 pairs of planes mentioned in § 4 of the pencil of cones  $K^2$  with vertex  $A$  have as images 3 points  $H_{ij} = H_{kl}$  of  $\Sigma_5$ , which lie resp. on the 3 quadratic surfaces  $\Omega_{ij}$ . The 3 points  $H_{ij}$  lie on the line  $\varrho_0$ . In this way we have determined the  $\Omega_{ij}$ , as they are defined by the points  $H_{ij}$  and the said skew quadrilaterals.

8. Now we can find something more about the planes  $\nu(P)$  of  $\Sigma_5$  mentioned in § 6. Let  $P$  be a point of  $R_3$ . The cones  $L^2$  with vertex  $P$  form a pencil which is represented as a straight line  $\varrho(P)$  of  $\Sigma_5$ . Among them there is a cone  $L^2$  which is formed by the planes  $PA_i A_j$  and  $PA_k A_l$ ; accordingly this  $L^2$  is represented as a point of  $\Omega_{ij}$ . As the plane pencil associated to this  $L^2$  has  $P$  as carrier, we find:

*Any plane  $\nu(P)$  of  $\Sigma_5$ , image of the sheaf of plane pencils  $(P)$ , cuts any  $\Omega_{ij}$  in one point. These 3 points of intersection are collinear.*

9. Now we shall try to find the images of the  $\infty^4$  pencils  $(P, \pi)$  of which  $\pi$  passes through a given point  $P_0$ . The associated  $O^2$  must satisfy the necessary and sufficient condition that  $A$  and  $P_0$  are conjugated, hence:

*The  $\infty^4$  plane pencils of which the planes pass through a given point  $P_0$ , have as images in  $\Sigma_5$  the points of a plane four-dimensional space  $V(P_0)$  through the straight line  $\varrho_0$ . That  $V(P_0)$  passes through  $\varrho_0$  results from the fact that any  $K^2$  of the pencil of cones with vertex  $A$  produces all the plane pencils of which the vertices lie on the associated  $\lambda$ , hence even an infinite number of pencils with planes through  $P_0$ .*

In the same way we have:

*the  $\infty^3$  pencils of which the planes pass through a given line  $l$ , have as images in  $\Sigma_5$  the points of a plane three-dimensional space  $D(l)$  through the line  $\varrho_0$ .*

In this way the  $\infty^4$  straight lines of  $R_3$  are represented in the plane three-dimensional spaces through a fixed straight line of  $\Sigma_5$ , hence also on a plane four-dimensional space.

10. Let us consider all plane pencils  $(P, \pi)$  for which  $P$  is fixed and  $\pi$  turns round a straight line  $l$  through  $P$ .  $O^2$  must satisfy the necessary and sufficient condition that  $P$  is the pole of  $a$  and that the polar plane of  $A$  passes through  $l$ ; hence:

*The  $\infty^1$  pencils with fixed vertex  $P$  of which  $\pi$  contains a given straight line  $l$  through  $P$  (a pencil of pencils  $[P, l]$ ), are represented in  $\Sigma_5$  as the points of a straight line  $\varrho(P, l)$  lying in the plane  $\nu(P)$ .*

Hence the  $\infty^5$  pencils of pencils are represented as the  $\infty^5$  straight lines of the  $\infty^3$  planes  $\nu(P)$ .

11. To an arbitrary straight line  $\varrho$  of  $\Sigma_5$  there correspond a pencil of conics in  $\alpha$  and a pencil of  $O^2$  in  $R_3$ . The polar planes  $\pi$  of  $A$  relative to this  $O^2$  pass through a fixed straight line  $l$ , and the pole of  $\alpha$  describes a cubic  $\gamma$  which cuts  $l$  twice. Hence: *to an arbitrary straight line of  $\Sigma_5$  there corresponds a set of plane pencils  $(P, \pi)$  in which  $P$  describes a cubic  $\gamma$  and  $\pi$  passes through a fixed chord of  $\gamma$ .*

12. We try to find the surface  $\Omega(l)$  in  $\Sigma_5$  which represents the  $\infty^2$  plane pencils  $(P, \pi)$  where  $P$  describes a line  $l$  and  $\pi$  turns round  $l$ .  $\Omega(l)$  lies in  $D(l)$ . The image of a straight line of  $D(l)$  in  $R_3$  is a pencil  $O^2$ , of which all the individuals have the property that the polar plane of  $A$  passes through  $l$ . The locus of the poles of  $\alpha$  is a cubic which cuts  $l$  twice; hence  $\Omega(l)$  is a quadratic surface. The straight line  $l$  cuts  $A^2$  twice; hence  $\Omega(l)$  cuts  $\varrho_0$  in two points. Let the plane  $\alpha_i$  cut  $l$  in  $L_i$ . There exists a plane through  $A_i L_i$  which, together with  $\alpha_i$ , forms an  $O^2$  for which the plane  $(A_i, l)$  has the point  $A$  as pole. Consequently  $\Omega(l)$  cuts each of the 4 planes  $\nu_i$  in one point. The space  $D(l)$  cuts  $\Omega_{ij}$ , besides in  $H_{ij}$ , in one more point. This point is the image of a pair of planes  $O^2$  of which the line of intersection  $s$  rests on  $l$  and for which the plane  $(s, l)$  is the polar plane of  $A$ ; accordingly the pencil  $(s, l)$  is associated to it; we see that  $\Omega(l)$  cuts the surfaces  $\Omega_{ij}$ . Hence:

*The quadratic surfaces  $\Omega(l)$  lie in the three-dimensional spaces  $D(l)$  through  $\varrho_0$ .  $\Omega(l)$  cuts each of the 4 planes  $\nu_i$  in their points of intersection with  $D(l)$  and each of the 3  $\Omega_{ij}$  in the points where they cut  $D(l)$  outside  $\varrho_0$ .)*

13. Let us now consider the  $\infty^3$  cones with vertices in  $\alpha$  and their images in  $\Sigma_5$ . The vertices of the cones of a net  $O^2$  form a curve of the order 6 so that the net contains 6 cones with vertices in  $\alpha$ . Accordingly the  $\infty^3$  cones with vertices in  $\alpha$  are represented as the points of a  $V_3^6$  in  $\Sigma_5$ . This  $V_3^6$  passes through  $\varrho_0$ , through the 3 quadratic surfaces  $\Omega_{ij}$  and the 4 planes  $\nu_i$ .  $V_3^6$  contains the images of the pencils of cones with vertices in  $\alpha$  and consists, therefore, of  $\infty^2$  straight lines. By the aid of this  $V_3^6$  we can find more about the  $\infty^3$  planes  $\nu(P)$  of  $\Sigma_5$  and about the  $\Omega(l)$ . Consider an arbitrary pencil  $O^2$  in the net for which each individual has  $P$  as pole of  $\alpha$ . This pencil contains 3 cones with vertices in  $\alpha$ . These cones are represented as 3 collinear points of  $V_3^6$ . Let, inversely,  $t$  be a trisecant of  $V_3^6$ . It represents a pencil  $O^2$  which contains 3 cones with vertices in  $\alpha$ . If  $P$  is the vertex of the 4<sup>th</sup> cone of the pencil,  $P$  is the pole of  $\alpha$  for all the individuals of the pencil; hence  $t$  lies in  $\nu(P)$ . Consequently (cf. § 10):

*The straight lines  $\varrho(P, l)$  of  $\Sigma_5$ , images of the  $\infty^5$  pencils of pencils  $[P, l]$  of  $R_3$ , are the  $\infty^5$  trisecants of  $V_3^6$ .*

<sup>1)</sup> It is obvious that for "Vereinigte Lage" of two plane pencils it is necessary and sufficient that their image points in  $\Sigma_5$  lie on the same  $\Omega(l)$ .

The planes  $\nu(P)$  of  $\Sigma_5$ , images of the  $\infty^3$  sheaves of pencils of  $R_3$ , are the  $\infty^3$  planes which are formed by those trisecants.

14. Now we shall explain the two systems of straight lines on each  $\Omega(l)$ . One system consists of the images of the pencils of pencils  $[P, l]$  if  $P$  describes the line  $l$ . Accordingly  $\Omega(l)$  consists of  $\infty^1$  trisecants of  $V_3^6$ . In order to explain the other system, we consider an arbitrary straight line  $l'$  through  $A$  in  $a$ . The  $O^2$  for which  $l$  and  $l'$  are associated, form a pencil. And as the plane pencils that correspond to all the individuals, contain  $l$ , the pencil is represented as a straight line of  $\Omega(l)$ . If  $l'$  turns round  $A$  in  $a$ , there arise  $\infty^1$  pencils of which the images in  $\Sigma_5$  are the straight lines of the second system on  $\Omega(l)$ . In particular we find:

*All the  $\Omega(l)$  consist of  $\infty^1$  trisecants of  $V_3^6$ .*

We may also say:

*The surfaces  $\Omega(l)$  consist of the trisecants of  $V_3^6$  that lie in the 3-dimensional spaces  $D(l)$  through  $\varrho_0$ .*

Let us mention one more property: the  $\Omega(l)$  corresponding to the rays  $l$  of the pencil  $(A, a)$ , are split up into 2 planes of which one is fixed, to wit the plane of  $\Sigma_5$  which represents the net  $O^2$  touching  $a$  in  $A$ .

**Mathematics.** — “*A Representation of the Linear Complex of Rays.*”

By Prof. JAN DE VRIES.

(Communicated at the meeting of March 28, 1925).

§ 1. In order to arrive at a simple representation of the linear complex of rays  $\mathbf{L}$ , we choose two lines  $a$  and  $b$  that are no complex rays, as double lines of a skew involution. Further we choose a point  $C$  so that the transversal  $t_c$  through  $C$  cutting  $a$  and  $b$ , does not belong to  $\mathbf{L}$ .

To a complex ray  $r$  there corresponds a line  $l$  in the involution in question: the transversal  $t$  through  $C$  cutting  $l$  and  $r$ , defines on  $r$  a point  $S$  which we consider as the *image* of  $r$ .

If  $S$  is an arbitrary point,  $\sigma$  its null plane and  $(L, \lambda)$  the plane pencil which is homologous with the plane pencil  $(S, \sigma)$ ,  $S$  is the image of the ray in  $\sigma$  that corresponds to the ray  $l$  which rests on  $CS$ .

§ 2. *Singular rays.* *a.* If  $l$  passes through  $C$ ,  $S$  is an arbitrary point of  $r$ ; this ray belongs to the plane pencil that has the point  $C^*$  associated to  $C$ , as vertex. Accordingly all the rays  $r^*$  in the null plane  $\gamma^*$  of  $C^*$  are *singular* and the plane pencil  $(C^*, \gamma^*)$  is its own image.

*b.* If  $r$  lies in the plane  $(Ca)$ , and accordingly cuts  $l$ ,  $S$  is an arbitrary point of  $r$ . Hence the rays  $r_a$  in  $\varrho_a = (Ca)$  and  $r_b$  in  $\varrho_b = (Cb)$  are *singular* and the plane pencils  $(R_a, \varrho_a)$  and  $(R_b, \varrho_b)$  are their own images.

*c.* The complex rays  $r_0$  resting on  $a$  and  $b$ , are *singular*, for  $l_0$  coincides with  $r_0$ , so that  $S$  becomes indefinite. The singular rays  $r_0$  form a *quadratic scroll*  $(r_0)^2$ .

§ 3. *Image of a plane pencil.* If the plane pencil  $(L, \lambda)$  is associated to the plane pencil  $(R, \varrho)$ , the transversals  $t$  form a quadratic cone. Hence the image of  $(R, \varrho)$  is a *conic*  $\varrho^2$ . The points of intersection  $A$  and  $B$  of  $\varrho$  with  $a$  and  $b$  lie on  $\varrho^2$ .

The conic  $\varrho^2$  degenerates into a *pair of lines* whenever the plane pencil contains a singular ray, hence a ray  $r^*$ ,  $r_a$ ,  $r_b$  or  $r_0$ ; in this case the images of the other rays lie on a straight line  $u$ .

The plane pencil can also contain *two singular rays*; in this case the vertex  $R$  is the image of all the other rays, hence a *singular point*.

§ 4. *Singular points.* *a.* If  $R$  lies on  $t_c$ ,  $t_c$  contains also the homologous point  $L$ ; the image of  $(R, \varrho)$  consists of two rays  $r_a$  and  $r_b$ .

Hence any point of  $t_c$  is *singular*. The points  $C$  and  $C^*$  belong to this group.

*b.* If  $A$  is a point of  $a$ , the plane pencil  $(A, a)$  contains a ray  $r_0$  and a ray  $r_a$ . Accordingly all points of  $a$  and  $b$  are *singular*.

*c.* If the plane  $\varrho_0$  of a pencil passes through  $C^*$  and through a ray  $r_0$ , the image consists of  $r_0$  and a ray  $r^*$  and the vertex  $R_0$  is a *singular* point. Any ray  $r^*$  cuts two rays  $r_0$ ; the locus of the *singular* points  $R_0$  is, therefore, a conic  $\sigma^2$  in  $\gamma^*$ .

The plane  $\varrho_0$  envelops a quadratic cone. Each of the two planes  $\varrho_0$  through an arbitrary point  $P$  contains a plane pencil with vertex  $R_0$ . The complex rays that rest on  $\sigma^2$ , form a congruence [2,2].

In the plane  $(Ca)$  lies  $t_c$ , hence  $C^*$ ; accordingly it contains a ray  $r^*$  and also a ray  $r_0$ , hence a point  $R_0 = R_a$ . Consequently the vertex of the plane pencil  $(R_a, \varrho_a)$  lies on  $\sigma^2$ ; the line  $C^*R_a$  cuts  $\sigma^2$  besides in the intersection of  $a$  with the plane  $\gamma^*$ .

§ 5. The conics  $\varrho^2$  rest on  $a$ ,  $b$ ,  $t_c$  and twice on  $\sigma^2$ . The line  $u_0$  which forms with a singular ray  $r_0$  the image of a plane pencil, rests on  $t_c$  and on  $\sigma^2$ , for  $r_0$  cuts  $a$ ,  $b$  and  $\sigma^2$ . Consequently the lines  $u_0$  form a congruence [2,2] with directrices  $t_c$  and  $\sigma^2$ .

The lines  $u^*$ , which complete a ray  $r^*$  to a  $\varrho^2$ , rest on  $a$  and  $b$  and form, accordingly, a congruence [1,1].

The lines  $u_a$  rest on  $b$  and on  $\sigma^2$ , for a ray  $r_a$  cuts  $a$ ,  $t_c$  and  $\sigma^2$  (in  $R_a$ ); hence the rays  $u_a$  form a congruence [1,2] with directrices  $b$  and  $\sigma^2$ .

§ 6. A *field of points*  $[S]$  is the *image* of a congruence [2,2]. For the two points of intersection of a  $\varrho^2$  with the plane  $\Sigma$  of  $[S]$  are the images of two rays  $r$  in the plane  $\varrho$ . This [2,2] contains *sixteen plane pencils*. In the first place the complex plane pencil of  $\Sigma$  of which the image lies in  $\Sigma$ .  $\Sigma$  contains further two lines  $u_a$ , two lines  $u_b$  and one line  $u^*$ ; the *seven* pairs of lines to which they belong, are the images of as many plane pencils of [2,2].  $\Sigma$  contains *five* singular points; consequently the congruence [2,2] contains a plane pencil  $(A, a)$ , a plane pencil  $(B, \beta)$ , a plane pencil with vertex on  $t_c$  and two plane pencils  $(R_0, \varrho_0)$ . Finally the point ranges on the intersections of  $\gamma^*$ ,  $\varrho_a$  and  $\varrho_b$  are the images of the plane pencils  $(C^*, \gamma^*)$ ,  $(R_a, \varrho_a)$  and  $(R_b, \varrho_b)$ .

§ 7. *Image of a net of rays*. The rays of  $L$  resting on a line  $d$ , also cut the polar line  $d'$  of  $d$ . Any plane  $\varrho$  through  $d$  contains a plane pencil, hence a conic  $\varrho^2$  that cuts  $d'$ .

Accordingly the *image* of a bilinear congruence is a *cubic* surface  $\Sigma^3$  through the lines  $d$  and  $d'$ ; it contains, besides, the lines  $a$ ,  $b$ ,  $t_c$  and the conic  $\sigma^2$ .

A *parabolic net of rays* with directrix  $r$  is represented by a cubic *monoid* that has the image  $S$  of  $r$  as double point.

§ 8. Two surfaces  $\Sigma^3$  have a *rational twisted curve*  $g^4$  in common besides  $a$ ,  $b$ ,  $t_c$  and  $\sigma^2$ ; it is the *image* of a *quadratic scroll*  $(r)^2$ . It has the lines  $a$ ,  $b$  and  $t_c$  as *bisecants*, for on each of these lines there rest two rays of  $(r)^2$ . It has four points in common with  $\sigma^2$ .

§ 9. A *point range*  $(S)$  is the image of a *cubic scroll*  $(r)^3$ , for the locus  $g$  of  $(S)$  meets three lines  $r$  that have their images on the surface  $\Sigma^3$  corresponding to a  $[1,1]$  and, accordingly, cut the directrix  $d$  lying on that surface.

As  $g$  is the single directrix of  $(r)^3$ , the polar line  $g'$  of  $g$  must be the double directrix.  $(r)^3$  contains the conic  $\sigma^2$ , for any plane pencil with vertex  $R_0$  contains a ray resting on  $g$ . For the same reason  $a$ ,  $b$  and  $t_c$  lie on  $(r)^3$ .

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**Mathematics.** — "The Triple Involution of Reye". By Prof. JAN DE VRIES.

(Communicated at the meeting of April 25, 1925).

1. The congruence of the twisted cubics through five points  $B_k$  defines in an arbitrary plane  $V$  the triples of an involution that has been examined by REYE<sup>1)</sup>. The tangent  $c$  at  $B_5$  to the curve  $\varrho^3$  which cuts  $V$  in a triple  $C_1, C_2, C_3$ , meets  $V$  in the point  $C$ , which we consider as the image of the group  $(C)$ . For this representation the intersections  $S_{k5}$  of the lines  $B_5 B_k$  and  $V$  are singular; for  $B_5 B_k$  forms a degenerate  $\varrho^3$  with any conic  $\varrho^2$  of the pencil in the plane  $B_h B_l B_m$  that has the points  $B_h, B_l, B_m$  and the passage of  $B_5 B_n$  as base points. Accordingly the point  $S_{k5}$  is the image of all the triples formed by  $S_{k5}$  and the pairs of the involution which are the intersections of these conics and the line  $b_{hlm} \equiv S_{hl} S_{hm} S_{lm}$ .

2. If  $C$  describes the straight line  $l$ , the curves  $\varrho^3$  that touch the plane  $B_5 l$  at  $B_5$ , describe a surface  $A$  that has only components of degenerate figures in common with the plane  $B_1 B_2 B_3$ . Through  $B_3, B_4, B_5$  there passes a  $\varrho^2$  that touches the plane  $B_5 l$  at  $B_5$  and cuts  $B_1 B_2$ . In accordance with this the intersection of  $A$  and the plane  $B_1 B_2 B_3$  consists of the straight lines  $B_1 B_2, B_1 B_3$ , and  $B_2 B_3$ , and  $A$  is a quadrinodal cubic surface through the edges of the tetrahedron  $B_1 B_2 B_3 B_4$  and the point  $B_5$ . Accordingly, as  $A$  is defined by two points  $C$ , hence by two triples  $(C)$ :

"Any two triples of the involution of triples define with the passages  $D_{kl}$  of the edges of  $B_1 B_2 B_3 B_4$  a cubic  $\lambda^3$  that contains an infinite number of other triples".

The curves  $\lambda^3$  form a net that has the angular points  $D_{kl}$  of a complete quadrilateral as base points. To this net belongs the configuration consisting of the line  $D_{12} D_{34}$  and a definite conic  $\lambda^2$ . The corresponding surface  $A$  consists of the curves  $\lambda^3$  that rest on  $D_{12} D_{34}$ <sup>2)</sup>.

3. If we define  $A^3$  by a point on the line  $b_{123}$  and another point chosen at random in  $V$ ,  $A^3$  consists of the plane  $B_1 B_2 B_3$  and a quadratic cone with vertex  $B_4$ . For the straight line  $l$  passes through the point  $S_{45}$ , so that  $A^3$  contains all the conics  $\varrho^2$  in  $B_1 B_2 B_3$ . Disregarding the groups

<sup>1)</sup> Geometrie der Lage, 3e Auflage, p. 225.

General considerations of triple-involutions in the plane are found in my paper on "cubic involutions". (These Proceedings 16, p. 974—987).

<sup>2)</sup> The curves  $\varrho^3$  which cut an arbitrary straight line, form a surface of the 5th order with triple points in  $B_k$ . Here it is replaced by  $\Lambda^3$  and the planes  $B_1 B_2 B_5, B_3 B_4 B_5$ .

(C) consisting of  $S_{45}$  and the pairs of the involution that lies on  $b_{123}$ , the point range on  $l$  is the image of an infinite number of triples lying on a  $\varrho^2$ .

"Any conic through the points  $D_{14}$ ,  $D_{24}$ ,  $D_{34}$ ,  $S_{45}$  contains an infinite number of groups of the involution of triples."

As any of the five points  $B$  can be the vertex of the sheaf that produces the representation, there are *ten* pencils ( $\lambda^2$ )<sup>1)</sup>.

4. If the image point  $C$  describes a conic  $\gamma^2$ , the corresponding curves  $\varrho^3$  describe a surface  $I^6$  with quadruple points  $B_1, B_2, B_3, B_4$ , double point  $B_5$  and double lines in the edges of  $B_1 B_2 B_3 B_4$ . For the plane  $B_3 B_4 B_5$  contains two conics  $\varrho^2$  which touch a generatrix of the cone that projects  $\lambda^2$  out of  $B_5$ ; hence  $B_1 B_2$  is a double line of  $I'$  etc.

The intersection of  $I'$  and  $V$  is a curve  $\gamma^6$  with 6 double points  $D_{kl}$ , which contains an infinite number of triples (C).

If  $\gamma^2$  passes through  $S_{45}$ ,  $I'$  contains the figures of which  $B_4 B_5$  is a component part and we find a curve  $\gamma^5$  with three double points, which contains an infinite number of triples. Etc.

Finally any  $\gamma^2$  through the four singular points  $S_{k5}$  contains an infinite number of triples each of which has a point of  $\gamma^2$  as image.

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<sup>1)</sup> Cf. W. VAN DER WOUDE, *The Cubic Involution of the First Rank in the Plane*. (These Proceedings 12, p. 751).

**Chemistry.** — “Equilibria in the system Zinc sulphate-Water”. By Prof. ERNST COHEN and Dr. A. L. TH. MOESVELD.

(Communicated at the meeting of February 28, 1925).

1. In connection with the theory of the so-called “Transition elements” ERNST COHEN, some twenty five years ago, carried out a number of solubility determinations for the system zinc sulphate-water <sup>1)</sup>, at temperatures between  $-5^{\circ}$  C. and the transition temperature.

These determinations, mentioned in Table 1, were in good agreement with the experiments carried out by CALLENDAR and BARNES at about the same time <sup>2)</sup>. The latter also embrace the temperature interval, lying between the transition temperature ( $39^{\circ}$ ) and  $50^{\circ}$  C.

TABLE I.

Temp.	Solubility of $Zn SO_4 \cdot 7 H_2O$ .				Solubility of $Zn SO_4 \cdot 6 H_2O$ .			
	1st Determination.	2nd Determination.	mean COHEN.	CALLENDAR and BARNES.	1st Determination.	2nd Determination.	mean COHEN.	CALLENDAR and BARNES.
$-5^{\circ}$	39.33	39.27	39.30	—	47.08	—	47.08	—
$0^{\circ}.1$	41.94	41.92	41.93	41.85	49.53	49.44	49.48	—
$9^{\circ}.1$	47.11	47.07	47.09	46.96	—	54.20	54.20	—
$15^{\circ}.0$	50.83	50.94	50.88	50.74	57.09	57.20	57.15	—
$25^{\circ}.0$	57.94	57.87	57.90	57.95	63.74	—	63.74	63.74
$30^{\circ}.0$	—	—	—	61.92	65.80	65.84	65.82	65.65
$35^{\circ}.0$	66.59	66.63	66.61	66.61	67.99	—	67.99	67.94
$39^{\circ}.0$	70.00	70.09	70.05	70.05	—	70.08	70.08	70.02

COHEN at the same time, pointed out that the solubility curve of the heptahydrate of zinc sulphate between  $-5^{\circ}$  and  $39^{\circ}$  C. may be represented by the equation

$$L_1 = 41.80 + 0.522t + 0.00496t^2 \dots \dots \dots (1)$$

while the observations of CALLENDAR and BARNES for the hexahydrate between  $39^{\circ}$  and  $50^{\circ}$  C. may be represented by the equation:

$$L_2 = 59.34 + 0.0054t + 0.00695t^2 \dots \dots \dots (2)$$

<sup>1)</sup> Zeitschr. f. physik. Chemie **34**, 179 (1900).

<sup>2)</sup> Proceedings Royal Society London **62**, 117 (1897).

The values in the last column of Table 1 were calculated by means of this equation. In either equation  $L$  represents the number of grammes  $ZnSO_4$ , present at  $t^\circ$  in 100 gr. of water. Moreover, COHEN pointed out, that the curve (2) gives a good agreement as regards the solubility of the hexahydrate up to  $25^\circ C$ .

In an investigation, lately published by CHARLES R. BURY <sup>1)</sup>, the study of the equilibrium in the system zinc sulphate-water was again taken up. His results, given in fig. 1, may be summarized as follows:

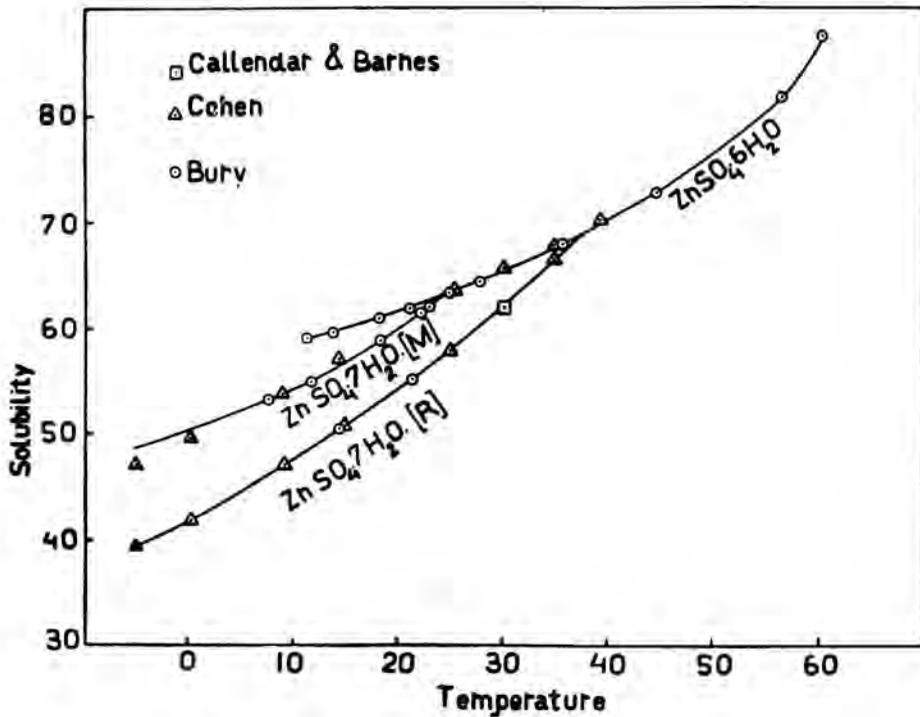


Fig 1.

Between  $40^\circ$  and  $50^\circ C$ . the agreement with the data of CALLENDAR and BARNES was satisfactory. COHEN's figures between  $39^\circ$  and  $25^\circ C$ . (meta-stable interval of the hexahydrate) agree with BURY's. Below  $25^\circ C$ . the values of the solubility of the hexahydrate found by COHEN lie on another curve than those found by BURY for the hexahydrate. They evidently refer to another hydrate.

Below  $11^\circ C$ . the hexahydrate changes spontaneously and irreversibly into the monoclinic heptahydrate. The latter is most easily obtained by spontaneous crystallisation of supersaturated solutions at about  $-10^\circ C$ .

<sup>1)</sup> Journ. chem. Soc. London **125**, 2538 (1924).

The values found by BURY for the solubility of this monoclinic heptahydrate are, between 7° and 23° C., in very close agreement with those given by COHEN<sup>1)</sup> for the hexahydrate in this interval. The monoclinic heptahydrate is metastable at all temperatures with respect to the rhombic heptahydrate. According to BURY the (metastable) monoclinic heptahydrate passes into the metastable hexahydrate at  $24^{\circ}.8 \pm 0.3$ .

3. We wish to observe here that already SCHROEDER<sup>2)</sup>, and later on LECOQ DE BOISBAUDRAN<sup>3)</sup> and also STORTENBEKER<sup>4)</sup> have described the monoclinic heptahydrate.

4. In the first place we shall now, by means of another procedure than BURY used, show that his statement, mentioned in 2 (in italics) is perfectly accurate and that therefore COHEN has not determined the solubility of the hexahydrate along the whole range of temperature  $-5^{\circ}$  up to  $39^{\circ}$  and  $50^{\circ}$  C., as he thought, but that in a part of this interval ( $-5^{\circ}$  up to  $23^{\circ}$  C.) another hydrate, probably the metastable monoclinic heptahydrate played the part of solute.

5. This proof, which, as will be shown, can be given very clearly, is drawn from a paper by COHEN: "Eine neue Methode zur Bestimmung von Umwandlungstemperaturen"<sup>5)</sup>.

In an apparatus, especially made for that purpose, he determined between  $-5^{\circ}$  and  $+50^{\circ}$  C. by means of a dipping electrode (F. KOHL-RAUSCH) the electrical resistance of saturated solutions of zinc sulphate.

In Table 2 as well as in Fig. 2, taken from COHEN's paper, the results of these measurements are given. In Fig. 2 the curves *CB* and *BA'* relate to the hexahydrate, *BA* to the heptahydrate.

The value of the resistance measured (point X) which, at  $25^{\circ}$  C., according to Table 2 would relate to the (at that temperature) metastable hexahydrate, falls far outside the curve *BA'*, and as this divergence lies far outside the experimental errors, the question arises, whether the points, furnished by the experiments between *A'* and *C*, really belong to one single continuous curve, or whether we have here two curves, to one of which belongs point X.

6. In order to investigate this we proceeded as follows: it appears to be possible to find a curve representing in the temperature interval of  $25^{\circ}$ — $50^{\circ}$  C. the resistances measured as function of the temperature in

1) The italics are C. and M's.

2) Lieb. Ann. **109**, 35 (1859).

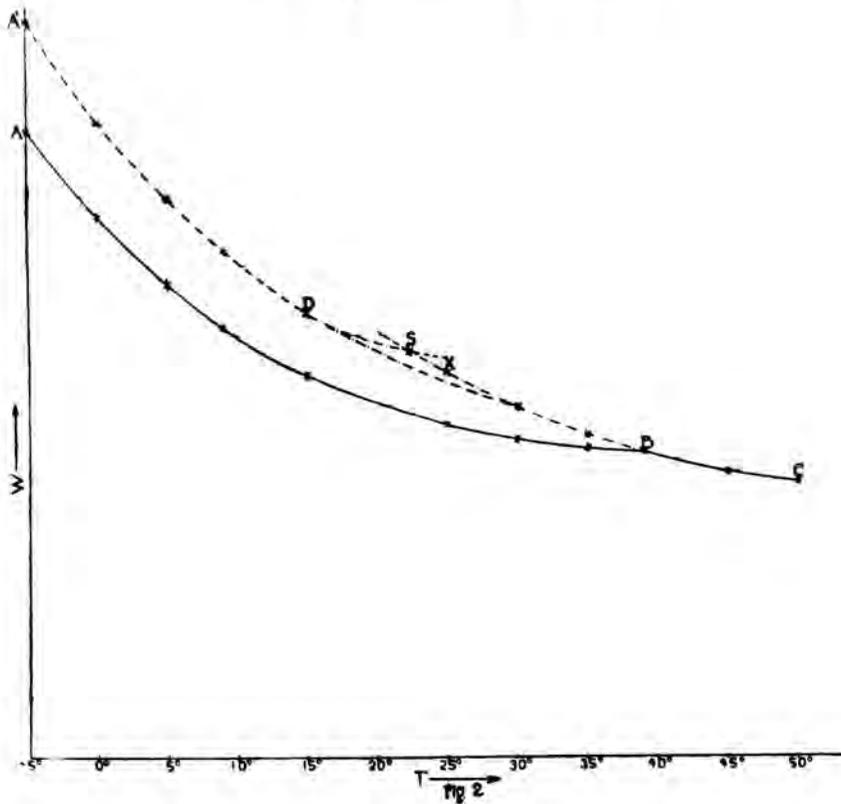
3) Ann. de chim. et de phys. (4) **18**, 266 (1869).

4) Zeitschr. f. physik. Chemie **22**, 60 (1897).

5) Zeitschr. f. physik. Chemie **31**, 164 (1899).

TABLE II.

Temperature.	Resistance of the solution.	
	Saturated with respect to $Zn SO_4 \cdot 7 H_2O$ .	Saturated with respect to $Zn SO_4 \cdot 6 H_2O$ .
— 5°.0	445.9	524.1
0.0	384.2	452.2
5.0	337.0	396.3
9.0	305.7	360.3
15.0	271.6	315.5
25.0	236.4	274.2
30.0	225.1	248.8
35.0	218.5	228.3
39.0	215.0	215.0
45.0	—	200.1
50.0	—	191.1



solutions in which the presence of the hexahydrate as a solute was supposed. From the values of Table 2, first and third columns we then find by means of the method of least squares the equation:

$$W_2 = 460.0 - 9.51t + 0.0828t^2 \dots \dots \dots (3)$$

From Table 3, fourth column, we see that this equation describes exactly the observations in this interval.

TABLE III.

<i>t.</i>	$W_{2found}$	$W_{2calc.}$	$W_{2found} - W_{2calc.}$
25°.0	274.2	274.0	- 0.2
30.0	248.8	249.1	+ 0.3
35.0	228.3	228.5	+ 0.2
39.0	215.0	215.0	± 0.0
45.0	200.1	199.7	- 0.4
50.0	191.1	191.4	+ 0.3

As the resistance measurements were made according to KOHLRAUSCH with a bridge wire of 1000 mm., a difference of 1 mm. in reading near the middle of the bridge corresponds with a difference of resistance of 0.4%. As is seen from column 4 of Table 3 this divergence is not reached anywhere.

If, on the contrary, using the values of resistance measured (Table 2, column 3) we try to calculate a curve for the temperature interval  $-5^\circ$  to  $25^\circ$  C., in which the point *X* is inserted, divergences appear between the values, given by the curve and the values, which have been experimentally determined, which lie far outside the errors of measurement.

If point *X* is not taken into consideration and with the method of least squares a curve is calculated by means of the figures of Table 2, column 3, between  $-5^\circ$  and  $15^\circ$  C. we find for that curve the equation:

$$W_1 = 453.8 - 12.70t + 0.2354t^2 \dots \dots \dots (4)$$

which, as is shown by Table 4 describes the observations most satisfactorily.

TABLE IV.

<i>t.</i>	$W_{1found}$	$W_{1calc.}$	$W_{1calc.} - W_{1found}$
$-5^\circ.0$	524.1	523.2	- 0.9
0.0	452.2	453.8	+ 1.6
5.0	396.3	396.2	- 0.1
9.0	360.3	358.6	- 1.7
15.0	315.5	316.2	+ 0.7

If, by means of (4) the value of the resistance at 25° C. is calculated, we find a value, which considerably differs from the one found experimentally (calc. 282.2; found 274.2).

7. The curves (3) and (4) therefore refer to the saturated solutions of two different substances (solutes). If the temperature of the intersection *S* of curves (3) and (4) is calculated we find for it 22° 5 C.

If we now take into consideration that BURY's values for the solubility of  $\text{ZnSO}_4 \cdot 7 \text{ aq.}$  monoclinic between 7° and 23° agree with those given by COHEN for  $\text{ZnSO}_4 \cdot 6 \text{ aq.}$  in this temperature interval, and that BURY has found  $24^\circ.8 \pm 0.3$  for the temperature of the intersection of the curves, which refer to  $\text{ZnSO}_4 \cdot 7 \text{ aq.}$  monoclinic and  $\text{ZnSO}_4 \cdot 6 \text{ aq.}$ , whereas our curves intersect at 22° 5 C. (curves (3) and (4)), it is highly probable, that curve (4) refers to  $\text{ZnSO}_4 \cdot 7 \text{ aq.}$  monoclinic, and is not, as COHEN thought the production of (3) and therefore does not refer to  $\text{ZnSO}_4 \cdot 6 \text{ aq.}$

If COHEN had examined in his apparatus the solute which was present at the determinations between -5° and +25° he would undoubtedly have perceived that he had to do with the monoclinic (metastable) hydrate of  $\text{ZnSO}_4 \cdot 7 \text{ aq.}$

8. BURY's researches on the one side furnish us with an explanation of the fact that the point *X*, found by COHEN in his resistance determinations falls totally outside the curve of the resistances, while on the other side the present point of view shows, that these resistance and solubility determinations by COHEN are in good agreement with BURY's results, if we apply the figures of the solubility and resistance found by COHEN below 25° C. to the (metastable) monoclinic hydrate  $\text{ZnSO}_4 \cdot 7 \text{ aq.}$  instead of to the (metastable)  $\text{ZnSO}_4 \cdot 6 \text{ aq.}$

9. The above demonstrates how important it is to mention "discrepant" results, when giving results of an investigation. In the case which we have discussed here, it is the mentioning of point *X*, (Fig. 2) which has facilitated the checking of the results, which have been obtained in a different way.

## SUMMARY.

It has been demonstrated that BURY's investigations on the equilibria in the system zinc sulphate-water, made by means of solubility determinations, give a complete explanation of the results, which at the time COHEN obtained by the same method as well as by means of determinations of resistance.

*Utrecht*, February 1925.

VAN 'T HOFF-Laboratory.

**Physics.** — “*On the light emitted by gases in the solid state and the spectrum of the northern light*”. By L. VEGARD, H. KAMERLINGH ONNES and W. H. KEESOM. (Communication from the physical laboratory at Leyden)<sup>1)</sup>.

(Communicated at the meeting of March 28, 1925).

This paper contains the results we obtained in the Leyden laboratory in cooperation with Mr. I. BERGE, and which form a continuation of the researches described by one of us in preceding communications<sup>2)</sup> on the light emitted by gases in the solid state.

After a series of investigations made at the temperature of liquid hydrogen, we observed the luminescence of different gases and gaseous mixtures at the temperature of liquid helium. We shall describe here especially the investigations on the light emitted when solid nitrogen and mixtures of nitrogen and neon at the temperature of *liquid helium* are bombarded by swift cathode rays.

From the light emitted by pure nitrogen at the temperature of liquid helium we obtained several spectra of high dispersion, which show, that the band  $N_1$  doubtlessly has the same structure and place as at the temperature of liquid hydrogen. In this case there is a principal maximum (5555) with two secondary maxima. This result is in correspondance with former observations made with liquid hydrogen under reduced pressure and shows that the *band  $N_1$  does not become narrower at lower temperatures*. The band  $N_2$  is strong, but is split up now into two components (5236, 5222).

Besides the bands  $N_1$  and  $N_2$  a *regular series of bands* is most prominent in this spectrum. Each band consists of a double line and a diffuse edge towards the red. In this respect they are different from the bands emitted by gaseous nitrogen. With the glass spectrograph used we obtained 7 bands on the plate, but doubtlessly these extend into the ultraviolet region.

The wavelengths are the following:

	1°.	2°.	3°.	4°.	5°.	6°.	7°.
strong	5770	5490	5116	4784	4490	4223	3986
weak		5502	5127	4795	4499	4231	3994.

<sup>1)</sup> A more detailed description will appear in one of the next “Communications” from the physical laboratory at Leyden.

<sup>2)</sup> L. VEGARD. These Proceedings 27. p. 113. Comm. from the phys. lab. at Leyden N<sup>o</sup>. 168d, C. R. t. 176 p. 974, t. 176 p. 1488, 1923, t. 178 p. 1153, t. 179 p. 35, t. 179 p. 151, 1924.

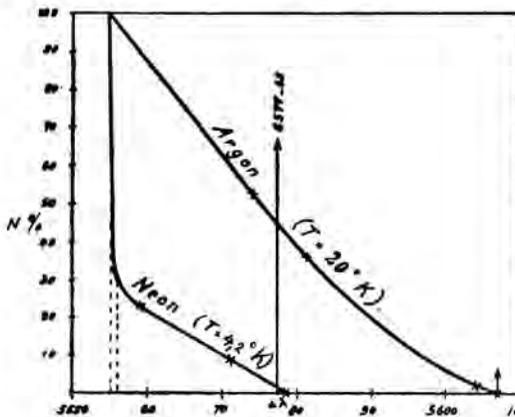
Undoubtedly we have here a state of development of the same bands that have already been observed at the temperature of liquid hydrogen and which became very strong with canal rays<sup>1)</sup>. At lower temperatures these bands, which at higher temperatures are very broad and diffuse, are contracted to narrow lines with a diffuse edge towards the read.

In argon containing traces of nitrogen and at the temperature of liquid hydrogen the bands are also contracted into two lines, but these lines have another position. The two strongest bands, corresponding to the fifth and the sixth band of the table, have the wavelengths: (4523, 4473) and (4231, 4211).

In a former communication one of us has remarked<sup>2)</sup>, that doubtlessly these two bands correspond with the bands observed by Lord RAYLEIGH in the diffuse light of the night sky, but as long as the wavelengths of the bands of Lord RAYLEIGH have not been determined more accurately we cannot say to which form of contraction they belong.

At the same temperature of liquid helium, nitrogen emits also three or four weak lines in the region of the great wavelengths viz. (5914, 5952, 6399) (6417?), which probably correspond to weak lines of the northern light spectrum.

The experiments with solid neon containing nitrogen in different



proportions have shown that the band  $N_1$  changes in a way similar to that found earlier for mixtures of nitrogen and argon<sup>3)</sup>.

A decrease of the concentration of the nitrogen brings the principal maximum to move towards greater wavelengths, while the secondary maxima finally disappear. This behaviour of nitrogen-neon mixtures

is similar to that of nitrogen-argon-mixtures, but as regards the magnitude of the displacement and the law it follows, the two kinds of mixtures show a very interesting and typical difference, which is illustrated by the figure. Here the wavelength of the principal maximum has been plotted as a function of the nitrogen concentration for the two mixtures. The shift of the principal maximum is caused by a specific action of the admixed gas on one side and by a decrease of the dimensions of the nitrogen particles on the other side.

For the argon mixtures at the temperature of liquid hydrogen the two

<sup>1)</sup> L. VEGARD. C.R. 179 p. 36.

<sup>2)</sup> loc. cit.

<sup>3)</sup> loc. cit.

influences are of the same order of magnitude. The specific action of the argon is evident from the fact that small argon concentrations cause a considerable shift of the principal maximum even when they cannot exert perceptible influence on the magnitude of the nitrogen particles.

For the nitrogen-neon-mixtures however the specific influence of the inert gas is very small. For neon concentrations varying from 0% up to 70% the position of the principal maximum remains nearly constant.

At this concentration the maximum begins to move quickly on account of the diminution of the nitrogen particles.

*In correspondance with the interpretation of the northern light spectrum formerly published by one of us, we see that when the nitrogen concentration approaches zero, the band  $N_1$  changes into a line with wavelength 5578.6 which nearly coincides with the green line of the northern light. According to this interpretation, this small difference  $\Delta \lambda = 1.2 \text{ \AA}$  should be accounted for by the specific influence of the neon.*

In neon containing traces of nitrogen the band  $N_2$  is split up into three components (5229—5220—5203) the first of which is the stronger one.

At increasing concentration of the nitrogen, the band  $N_2$  changes into a double line. Moreover the spectrum shows a number of lines perhaps belonging to the neon spectrum.

**Zoology.** — "Cross-breeding experiments with the three-and tenspined Stickleback (*Gasterosteus aculeatus* L. and *Gasterosteus pungitius* L.)." By Dr. G. J. VAN OORDT. (Communicated by Prof. J. BOEKE).

(Communicated at the meeting of May 30, 1925).

It is well-known that interspecific hybridization, even with closely related species, is accompanied by great difficulties. It is remarkable that in many fish-species this is not the case, however. Hybrids between different species, genera, families and even orders of fishes can be easily produced artificially. In most cases these hybrids prove to have great vitality; as a rule the more unrelated the parents are the sooner the hybrids die.

In this respect the experiments of several American investigators (e.g. MOENKHAUS 1904, BANCROFT 1912, MORRIS 1914, NEWMAN 1914, 1915, 1918, PINNEY 1918, 1922) as well as those of KAMMERER (1907), G. and P. HERTWIG (1914) a.o. are well-known. As appears from the investigations of GERSCHLER (1914) and BELLAMY (1922) some Cyprinodonts easily hybridize under natural conditions. These hybrids (*Platypoecilus* ♂ × *Xiphophorus* ♀ as well as the reciprocal cross) are absolutely fertile, *inter se* as well as with the parents.

Formerly it was tried to fertilize eggs of *Gasterosteus aculeatus* with sperm of other fish-species; but as far as I know, results were only obtained artificially. It was not only possible to cross *G. aculeatus* with the closely related *Spinachia vulgaris* (APPELLÖF 1894), but also to fertilize *G. aculeatus*-eggs with sperm of different (some far-related) species and genera (NEWMAN 1915). I do not know whether hybrids between the three closely related species *Gasterosteus aculeatus*, *G. pungitius* and *Spinachia vulgaris* have been obtained under natural conditions. Moreover, hybrids between *G. aculeatus* and *G. pungitius*, both common species in fresh water, are never found in nature. This must be ascribed to the markedly different breeding instincts of both species.

The males of these *Gasterosteus*-species make nests, in which the ♀♀ deposit their eggs. The male of *G. aculeatus* prepares a nest of small branches, leaves of waterplants, roots, sand-grains etc. which is situated at the bottom of the ditch or in the sand of the aquarium. The nest of *G. pungitius*, however, is fastened by preference at some distance from the bottom among dense vegetation. It is composed of about the same material (sand-grains excepted) as the nest of the three-spined Stickleback. In both species the nest material is fastened by means

of a secretion, formed by the kidney of the male fish, which hardens in water. The entrance of the nest of *G. pungitius* is at the side, that of *G. aculeatus* is situated closer to the upperside.

In both species the male tries to lure the ripe female into the nest or to chase it into it. When this succeeds the ♀ deposits its eggs in the nest and then the ♂ ejaculates its sperm over the ova. The male guards the nest, drives off all intruders fiercely and constantly conducts fresh water to the eggs by regularly and quickly moving its pectoral fins, while remaining at the entrance of the nest.

The nuptial colours of the males of both species differ markedly. That of *G. pungitius* is almost totally black; the ventral side of the ♂ of *Gasterosteus aculeatus* is brilliant red and the upper side a dark colour; moreover the iridescent eye of the ♂ is very conspicuous. The ♀♀ of *G. aculeatus* are generally paler than those of *G. pungitius*, which are markedly dotted; the depth of the body of the former is relatively greater than that of the latter. The number of dorsal spines of *G. aculeatus* is 3 (two large and one small one), that of *G. pungitius* varies from 9–11.

In the beginning of 1925 several aquaria were prepared, in two of which were placed one male of *G. pungitius* with some females of *G. aculeatus*, in two others one ♂ of *G. aculeatus* with some ♀♀ of *G. pungitius*. Moreover, several ♂♂ of *G. aculeatus* were placed in a larger tank with several ♀♀ of *G. pungitius*, while finally one ♂ of *G. pungitius* was put together with some ♀♀ of the same species. It was the intention to replace the latter by ripe ♀♀ of *G. aculeatus*, when the nest was ready. Care was taken of the size of the fishes being almost equal: generally the specimens of *G. aculeatus*, especially the ♀♀, are somewhat larger than those of *G. pungitius*.

In all cases the ♂♂ assumed their nuptial colouring and soon nest-building began. Though the ♂♂ behaved in the same way towards the ♀♀ of the other species as towards the ♀♀ of the own species, no eggs were laid in the nests, one case excepted. This exception will be described elaborately here.

A male of *Gasterosteus pungitius* was placed together with three females of *G. aculeatus* on April 1. On April 3 it began to make a nest among dense waterplants at about 25 cm. from the bottom of the aquarium. That same day two ♀♀, with swollen abdomens, deposited at the bottom of the aquarium an egg-mass, which was soon devoured by the male. On April 5 both these ♀♀ were dead. The male, which had chased the ♀♀ vigorously, continued chasing the remaining one. In the meantime the nest was completed. On April 9 the ♀ had markedly swollen gonads; it was so heavy that it had great difficulty in swimming and constantly sank to the bottom of the tank. The ♂ often concentrated its attention on the ♀, which remained near the bottom of the aquarium;

it tried to lure the ♀ to the nest, which was situated higher up, but the ♀ could not follow the ♂, owing to the heaviness of its body. In the afternoon of April 9 the relation had somewhat changed: I got the impression that now the ♀ tried to lure the ♂ to the bottom of the tank i. e. to the place, where the nest of *G. aculeatus* is normally found. Consequently a long battle arose.

On April 10 the ♀ had deposited its eggs, its abdomen being slender again. However, the eggs were not found at the bottom of the aquarium; so they must have been eaten or laid in the nest. The nest was not investigated in order not to disturb the ♂. On April 12 the ♀ again possessed a swollen abdomen; the male did not take notice of the nest; it came only a few times near it and only now and then conducted a small quantity of fresh water to it. It must be mentioned that before the eggs were in the nest, the ♂ did this continually. On April 14 the ♀ had deposited its eggs again. On investigating the nest, I found that it contained a great number of fertilized eggs with well developed germ-discs. Taking into consideration the developmental stage, I am of opinion that the eggs were laid on April 13.

Soon after the nest was taken away, the ♂ began to gather new material and on April 15 a new nest was ready. The ♂ also began to chase the ♀ more vigorously; hence it appears that the earlier breeding-instincts begin to show again after the nest has been destroyed.

The nest containing the eggs was placed in a tank with many water-plants. For the first days the mortality of the embryos was small, but soon increased and for that reason the living ova were further bred separately, and the nest was removed. On April 18 the optic vesicles were clearly perceptible; on April 20 pigment was visible in the eyes and the pulsating heart was conspicuous. On April 21 numerous melanophores were formed; then the blood-stream in the large yolk-veins was distinctly visible. On April 22 the first body-movements of the embryo, still in the egg-shell, were observed; then the mortality was so heavy that the few remaining living embryos were fixed (April 23).

The ♀ mentioned above once more showed a strongly swollen abdomen, owing to the numerous ripe eggs, but eggs were not laid in the nest anymore. In the other cases, in which a ♂ of *G. pungitius* and ♀♀ of *G. aculeatus* were put together, I had no success. The females of *G. pungitius*, which had been placed with a male of *G. aculeatus* never even laid eggs. The ♂♂ continually chased the females of the other species. The latter were very much afraid and hid as much as possible among the waterplants. The males of *G. aculeatus* always made a normal nest, however, and though these nests did not contain eggs the males regularly conducted fresh water to them with their pectoral fins. The males of both species never ejaculate their sperm spontaneously. In such „overripe“ males the abdomen swells, owing to the retention of the sperm.

I have already mentioned that in „overripe“ ♀♀ the abdomen was swollen as well. In a few cases I found that the ♀♀ of *G. aculeatus* with swollen abdomens, deposited their eggs at the bottom of the tank. Sometimes these females died soon after, sometimes they died without having deposited their ova. This was also observed in a few “overripe“ ♂♂ of *G. aculeatus* and *G. pungitius*. The possession of such overripe ovaria or testes seems to be very harmful for these specimens.

From the above it follows:

I. That the males of both *Gasterosteus aculeatus* and *G. pungitius* behave towards the females of the other species as if the latter belong to their own species. The fact that the females of *G. pungitius* are more afraid of a male of *G. aculeatus* than of a male of their own species is probably due to the male of *G. aculeatus* chasing them with greater vigour. The behaviour of the ♂♂ of *G. aculeatus* shows, however, that they do not consider the ♀♀ of *G. pungitius* to belong to another species.

II. That the males of both species begin to prepare nests in the presence of females of the other species.

III. That the strongly differing breeding-instincts of both species probably cause the non-despositing of the eggs in the nests of the other species. The case, described above, in which this did happen, was probably due to incidental circumstances.

IV. That the ♂ of *G. pungitius* appears to recognize its eggs only as such, when they are in the nest<sup>1)</sup>, for eggs found at the bottom of the aquarium are soon devoured by it.

V. That, when a nest with eggs of *G. pungitius* is taken away, the male at once begins to make a new nest and to chase females. When there are eggs in the nest the ♂ does not chase other specimens with as much vigour.

I cannot trace whether the hybrids thus obtained show characteristics of both parents or of one only, because they are too young in many respects. As the melanophores have developed, however, an investigation of the place where they are found and of the shape of these cells may perhaps decide this question. Moreover, the behaviour of the paternal and maternal chromatin will be traced. I think it very improbable that the eggs develop parthenogenetically, taking into consideration the investigations on other Teleost-hybrids.

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<sup>1)</sup> A similar case was described recently by PORTIELJE (1925) in the Nandu (*Rhea americana* L.) The eggs of this bird are incubated by the male only.

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**Mathematics.** — "On the binomial equation of prime degree". By  
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(Communicated at the meeting of April 25, 1925).

1. The roots of the equation

$$z^p - 1 = 0 \quad \dots \dots \dots (1)$$

where  $p$  is prime, can be expressed by radicals and the index of the radical signs involved is  $p-1$ . Likewise, putting  $p-1$  equal to  $v_1$ , the equation of degree  $v_1$ , the roots of which are the so-called GAUSSIAN periods of order  $v_1$ <sup>1)</sup>, admits of an algebraic solution, and the radical signs involved have the index  $v_1$ .

These GAUSSIAN periods are defined as follows. Let  $g$  be a primitive root of the prime number  $p$ ,  $a$  any complex root of the equation (1), then, putting

$$a_k = a_0^k \quad , \quad a_0 = a,$$

the periods of order  $v$  are the  $v_1$  sums

$$y_s = \sum_{k=0}^{k=v_1-1} a_{k v_1 + s},$$

$$(s = 0, 1, 2, \dots, v_1 - 1).$$

The method of finding the values of these periods is based upon the consideration of the sum

$$f(a, \gamma^\mu) = \sum_{k=0}^{k=p-2} a_k \gamma^{k\mu},$$

where  $\mu$  is any integer and  $\gamma$  represents a primitive root of the new binomial equation

$$z^{v_1} - 1 = 0. \quad \dots \dots \dots (2)$$

Evidently we have

$$\left. \begin{aligned} f(a, \gamma^{\mu_1}) &= f(a, \gamma^{\mu_2}), & \text{if } \mu_1 &\equiv \mu_2, \\ f(a, \gamma^\mu) &= -1, & \text{if } \mu &\equiv 0, \end{aligned} \right\} \pmod{v_1}$$

$$f(a_h, \gamma^\mu) = \gamma^{-h\mu} f(a, \gamma^\mu),$$

and we can prove

$$|f(a, \gamma^\mu)| = \sqrt[p]{p} \quad , \quad \text{if } \mu \equiv \not\equiv 0, \pmod{v_1}.$$

<sup>1)</sup> Disquisitiones arithmeticae (deutsch von H. MASER), Art. 343.

It is then readily seen that the expression

$$\frac{f(\alpha, \gamma^{\mu_1}) f(\alpha, \gamma^{\mu_2})}{f(\alpha, \gamma^{\mu_1+\mu_2})}$$

is a symmetric function of the roots  $\alpha_i$ , depending only on  $\mu_1, \mu_2$  and  $\gamma$ , and that, when we write

$$\frac{f(\alpha, \gamma^{\mu_1}) f(\alpha, \gamma^{\mu_2})}{f(\alpha, \gamma^{\mu_1+\mu_2})} = \psi_{\mu_1, \mu_2}(\gamma),$$

the righthand side will be in general a polynomial in  $\gamma$ .

Indeed, when we have  $\mu_1 \equiv 0, \mu_2 \equiv 0, \mu_1 + \mu_2 \equiv 0, \pmod{v_1}$ , it is possible to show that

$$\psi_{\mu_1, \mu_2}(\gamma) = \sum_{r_1, r_2} \gamma^{r_1 \mu_1 + r_2 \mu_2},$$

where  $r_1$  and  $r_2$  take all the values  $1, 2, 3, \dots, p-2$ , always remaining connected by the one to one relation

$$g^{r_1} + g^{r_2} \equiv 1, \pmod{p} \quad \dots \dots \dots (3)$$

Hence, in the general case,  $\psi_{\mu_1, \mu_2}(\gamma)$  is a sum of  $p-2$  terms, each of them being a certain power of the root  $\gamma$ , and from the definition it follows that at the same time we have

$$|\psi_{\mu_1, \mu_2}(\gamma)| = \sqrt{p}.$$

However, when  $\mu_1$  and  $\mu_2$  are not quite arbitrary, other results are obtained, and in particular we must note the equations

$$\psi_{\mu_1, \mu_2}(\gamma) = -1, \text{ if } \mu_1 \equiv 0, \text{ of als } \mu_2 \equiv 0 \pmod{v_1},$$

$$\psi_{\mu_1, \mu_2}(\gamma) = (-1)^{\mu_1 v_1 - 1} p = (-1)^{\mu_2 v_1 - 1} p, \text{ if } \mu_1 \equiv 0, \mu_2 \equiv 0, \mu_1 + \mu_2 \equiv 0 \pmod{v_1}.$$

Now, supposing one of the two indices to be equal to unity, we have in particular

$$\psi_{1, \mu}(\gamma) = G_{\mu}(\gamma) = \sum_{r_1, r_2} \gamma^{r_1 + \mu r_2}, \text{ if } \mu \equiv 0, \mu + 1 \equiv 0, \pmod{v_1}$$

and also  $\psi_{1, \mu}(\gamma^k) = G_{\mu}(\gamma^k) = \sum_{r_1, r_2} \gamma^{k(r_1 + \mu r_2)}, \text{ if } k\mu \equiv 0, k(\mu + 1) \equiv 0, \pmod{v_1}$  (4)

in which formulae  $r_1$  and  $r_2$  are still connected by the relation (3), and the special sum  $G_{\mu}(\gamma)$  will satisfy the relations

$$\left. \begin{aligned} G_{\mu_1}(\gamma) &= G_{\mu_2}(\gamma) & , & \text{ if } \mu_1 \equiv \mu_2, \\ G_{\mu}(\gamma) &= -1 & , & \text{ if } \mu \equiv 0, \\ G_{\mu}(\gamma) &= (-1)^{v-1} p & , & \text{ if } \mu + 1 \equiv 0, \end{aligned} \right\} \pmod{v_1} (5)$$

$$|G_{\mu}(\gamma)| = \sqrt{p}, \quad G_{\mu}(\gamma) = (-1)^{\mu} G_{-\mu-1}(\gamma), \text{ if } \mu \equiv 0, \mu + 1 \equiv 0, \pmod{v_1}$$

$$G_{\mu}(\gamma^k) = \frac{G_1(\gamma) G_2(\gamma) G_3(\gamma) \dots G_{(\mu+1)k-1}(\gamma)}{G_1(\gamma) G_2(\gamma) \dots G_{k-1}(\gamma) \cdot G_1(\gamma) G_2(\gamma) \dots G_{\mu k-1}(\gamma)} \dots (6)$$

Finally, it should be noticed that the sums  $f(a, \gamma^m)$  can be expressed by means of  $G_\mu(\gamma)$  and that we can establish the equations

$$\begin{aligned} f(a, \gamma)^m &= G_1(\gamma) G_2(\gamma) G_3(\gamma) \dots G_{m-1}(\gamma) f(a, \gamma^m), \\ f(a, \gamma)^{v_1} &= G_0(\gamma) G_1(\gamma) G_2(\gamma) \dots G_{v_1-1}(\gamma). \end{aligned} \quad (7)$$

Hence, as soon as the sums  $G_1(\gamma), G_2(\gamma), \dots, G_{v_1-1}(\gamma)$  are calculated, we find the value of  $f(a, \gamma)$  by extracting a  $v_1$ -th root, and subsequently we are able to determine  $f(a, \gamma^m)$  for any value of  $m$ .

Now, putting

$$v_1 y + 1 = \sum_{k=1}^{k=v_1-1} f(a, \gamma^k),$$

or

$$v_1 y + 1 = f(a, \gamma) + \sum_{k=2}^{k=v_1-1} \frac{f(a, \gamma)^k}{G_1(\gamma) G_2(\gamma) \dots G_{k-1}(\gamma)}, \dots (8)$$

and introducing successively into this formula the  $v_1$  values of  $f(a, \gamma)$ , we can show that the  $v_1$  values found for  $y$  are precisely the  $v_1$  GAUSSIAN periods  $y_s$  of the order  $v$ .

It should be noted that if we replace  $g$  by another primitive root of  $p$ , or  $\gamma$  by another primitive root of the equation (2) the formula (8) still gives the same results, only the order in which the  $v_1$  values of the periods  $y_s$  present themselves will be altered.

2. For a given large prime number  $p$  the calculation of the sums  $G_\mu(\gamma)$  by means of (4) is very laborious and almost impracticable, but when  $v_1$  is small, it is sometimes possible to form the equation of the  $v_1$ -th degree whose roots are the  $v_1$  periods. To this end, we must observe that this equation, the leading coefficient being unity, necessarily has real and integer coefficients, and we must have recourse to the theory of numbers. In this note I will show how to deduce the equation of the periods when  $v_1$  is 5 or 6, and how to solve it algebraically.

In the first place, let  $p = 10w + 1$  and  $v_1 = 5$ . then we have according to (5), (7) and (8)

$$\gamma^4 + \gamma^3 + \gamma^2 + \gamma + 1 = 0 \dots (9)$$

$$\begin{aligned} G_0(\gamma) &= -1, \quad G_2(\gamma) = G_1(\gamma^2), \quad G_3(\gamma) = G_1(\gamma), \quad G_4(\gamma) = -p, \\ G_1(\gamma^{-1}) &= \frac{p}{G_1(\gamma)}, \quad G_2(\gamma^{-1}) = \frac{p}{G_2(\gamma)}, \\ f(a, \gamma)^5 &= p G_1^2(\gamma) G_2(\gamma), \end{aligned} \quad \left. \vphantom{\begin{aligned} G_0(\gamma) &= -1, \quad G_2(\gamma) = G_1(\gamma^2), \quad G_3(\gamma) = G_1(\gamma), \quad G_4(\gamma) = -p, \\ G_1(\gamma^{-1}) &= \frac{p}{G_1(\gamma)}, \quad G_2(\gamma^{-1}) = \frac{p}{G_2(\gamma)}, \\ f(a, \gamma)^5 &= p G_1^2(\gamma) G_2(\gamma), \end{aligned}} \right\}$$

$$5y + 1 = f(a, \gamma) + \frac{f(a, \gamma)^2}{G_1(\gamma)} + \frac{f(a, \gamma)^3}{G_1(\gamma) G_2(\gamma)} + \frac{f(a, \gamma)^4}{G_1^2(\gamma) G_2(\gamma)}$$

or

$$5y + 1 = f(a, \gamma) + \frac{p}{f(a, \gamma)} + \frac{f(a, \gamma)^2}{G_1(\gamma)} + \frac{p G_1(\gamma)}{f(a, \gamma)^2}$$

and since  $|f(a, \gamma)| = |G(\gamma)| = \sqrt{p}$ , it appears that everyone of the five roots  $y$  is real. The equation of the periods  $F(y) = 0$  presents itself in the form

$$0 = \begin{vmatrix} \frac{5y+1}{\sqrt{p}} & 1 & \frac{G_1(\gamma^{-1})}{\sqrt{p}} & \frac{G_1(\gamma^{-1})G_2(\gamma^{-1})}{\sqrt{p^2}} & \frac{G_1^2(\gamma^{-1})G_2(\gamma^{-1})}{\sqrt{p^3}} \\ 1 & -\frac{5y+1}{\sqrt{p}} & 1 & \frac{G_1(\gamma^{-1})}{\sqrt{p}} & \frac{G_1(\gamma^{-1})G_2(\gamma^{-1})}{\sqrt{p^2}} \\ \frac{G_1(\gamma)}{\sqrt{p}} & 1 & -\frac{5y+1}{\sqrt{p}} & 1 & \frac{G_1(\gamma^{-1})}{\sqrt{p}} \\ \frac{G_1(\gamma)G_2(\gamma)}{\sqrt{p^2}} & \frac{G_1(\gamma)}{\sqrt{p}} & 1 & -\frac{5y+1}{\sqrt{p}} & 1 \\ \frac{G_1^2(\gamma)G_2(\gamma)}{\sqrt{p^3}} & \frac{G_1(\gamma)G_2(\gamma)}{\sqrt{p^2}} & \frac{G_1(\gamma)}{\sqrt{p}} & 1 & -\frac{5y+1}{\sqrt{p}} \end{vmatrix}$$

and expanding the determinant, we get

$$0 = (5y+1)^5 - 10p(5y+1)^3 - 5p(5y+1)^2 [G_1(\gamma) + G_1(\gamma^{-1}) + G_2(\gamma) + G_2(\gamma^{-1})] + 5p(5y+1) [p - \{G_1(\gamma) + G_1(\gamma^{-1})\} \{G_2(\gamma) + G_2(\gamma^{-1})\}] - p [G_1^2(\gamma)G_2(\gamma) + G_1^2(\gamma^{-1})G_2(\gamma^{-1}) + G_2^2(\gamma)G_1(\gamma^{-1}) + G_2^2(\gamma^{-1})G_1(\gamma)].$$

Now we put

$$G_1(\gamma) = \sqrt{p}e^{i\theta_1}, \quad G_2(\gamma) = \sqrt{p}e^{i\theta_2}, \quad S_1 = G_1(\gamma) + G_1(\gamma^{-1}) + G_2(\gamma) + G_2(\gamma^{-1}) = 2\sqrt{p}(\cos \theta_1 + \cos \theta_2),$$

$$S_2 = \{G_1(\gamma) + G_1(\gamma^{-1})\} \{G_2(\gamma) + G_2(\gamma^{-1})\} = 4p \cos \theta_1 \cos \theta_2,$$

$$\eta = 8p\sqrt{p} \sin \theta_1 \sin \theta_2 (\cos \theta_1 - \cos \theta_2),$$

whence we have the inequalities

$$|S_1| < 4\sqrt{p}, \quad |S_2| < 4p, \quad |\eta| < 16p\sqrt{p} \dots \dots (10)$$

Transforming the equation of the periods  $F(y) = 0$  and introducing  $S_1, S_2$  and  $\eta$  we get

$$0 = y^5 + y^4 - \frac{2}{5}(p-1)y^3 + \frac{1}{5^2}y^2(2-6p-pS_1) + \left. \begin{aligned} & + \frac{1}{5^3}y(1-6p+p^2-2pS_1-pS_2) + \\ & + \frac{1}{5^5} \left( 1 - 10p + 5p^2 - 5pS_1 + p^2S_1 - 5pS_2 - \frac{1}{2}pS_1S_2 + \frac{1}{2}p\eta \right) \end{aligned} \right\} (11)$$

in which equation, the prime number  $p$  being given, the three numbers  $S_1, S_2$  and  $\eta$  must be evaluated. To this end I proceed as follows.

The equation (4)

$$G_1(\gamma) = \sum_{r_1, r_2} \gamma^{r_1+r_2}$$

can be reduced to

$$G_1(\gamma) = Q_1 \gamma + Q_2 \gamma^2 + Q_3 \gamma^3 + Q_4 \gamma^4,$$

and as we have  $G_2(\gamma) = G_1(\gamma^2)$ , the sums  $G_2(\gamma)$ ,  $G_1(\gamma^{-1})$  and  $G_2(\gamma^{-1})$  are expressible by the same coefficients  $Q_h$  that necessarily are integers. Addition of  $G_1(\gamma)$ ,  $G_1(\gamma^{-1})$ ,  $G_2(\gamma)$  en  $G_2(\gamma^{-1})$  gives at once

$$\sum_1^4 Q_h = -S_1, \quad \dots \dots \dots (12)$$

hence  $S_1$  is an integer. Now writing  $t_h = \gamma^h + \gamma^{-h}$ , and noticing that we have

$$t_1 = t_4, \quad t_2 = t_3, \quad t_1 + t_2 = -1, \quad t_1 t_2 = -1, \quad (t_1 - t_2)^2 = 5,$$

the condition  $|G_1(\gamma)| = \sqrt{p}$  gives

$$p = \sum_1^4 Q_h^2 + t_1(Q_1 Q_2 + Q_2 Q_3 + Q_3 Q_4) + t_2(Q_1 Q_3 + Q_2 Q_4 + Q_4 Q_1).$$

But we have also  $|G_2(\gamma)| = \sqrt{p}$ , therefore we must conclude to

$$Q_1 Q_2 + Q_2 Q_3 + Q_3 Q_4 = Q_1 Q_3 + Q_2 Q_4 + Q_4 Q_1.$$

and to

$$2p = 2 \sum_1^4 Q_h^2 - \sum_{h,k} Q_h Q_k.$$

If we now put

$$Q_1 - Q_4 = X, \quad Q_2 - Q_3 = Y, \quad Q_1 + Q_4 - Q_2 - Q_3 = V$$

we have

$$\begin{aligned} G_1(\gamma) + G_1(\gamma^{-1}) - G_2(\gamma) - G_2(\gamma^{-1}) &= \\ &= (t_1 - t_2) V = 2 \sqrt{p} (\cos \theta_1 - \cos \theta_2), \quad \left| \frac{V}{5} \right| < \frac{4\sqrt{p}}{5\sqrt{5}} \end{aligned} \quad (13)$$

and consequently

$$S_1^2 - 4 S_2 = 5V^2 \quad \dots \dots \dots (14)$$

a formula showing that  $S_2$  is an integer and that  $S_1$  and  $V$  are both odd or both even.

Concerning the product

$$S_1 V = \frac{4p}{t_1 - t_2} (\cos^2 \theta_1 - \cos^2 \theta_2)$$

we may notice the inequality

$$\left| \frac{S_1 V}{5} \right| < \frac{4p}{5\sqrt{5}} \dots \dots \dots (15)$$

and prove the relation

$$- S_1 V = X^2 + 4XY - Y^2 = (X + 2Y)^2 - 5Y^2 = 5X^2 - (2X - Y)^2. \quad (16)$$

Finally we can deduce the equation

$$16p = 10X^2 + 10Y^2 + S_1^2 + 5V^2, \dots \dots \dots (17)$$

showing that for any prime number  $p = 10w + 1$  the number  $16p$  can be resolved into a peculiar sum of squares, a partition the possibility of which is not easily established in another way.

Now it is possible to show that the integer  $V$  is a multiple of 5. In fact, in equation (11) the coefficients of  $y^2$  and of  $y$  are integers. Hence we have in the first place

$$pS_1 \equiv 2 - 6p \pmod{25}$$

or

$$\begin{aligned} S_1 &\equiv -2(p+1) \pmod{25} \dots \dots \dots (18) \\ S_1 &\equiv +1 \pmod{5}. \end{aligned}$$

But we have also

$$pS_2 \equiv 1 - 6p + p^2 - 2p S_1 \pmod{125}$$

leading to

$$S_2 \equiv -1 \pmod{5}$$

and by combining the congruencies we will find

$$p^2(S_1^2 - 4S_2) = 5p^2V^2 \equiv 4(1-p)^3 \equiv 0 \pmod{25}$$

or

$$V \equiv 0 \pmod{5}.$$

Therefore we have from (16)

$$X + 2Y \equiv 0, \quad 2X - Y \equiv 0 \pmod{5}$$

and as

$$5(X^2 + Y^2) = (X + 2Y)^2 + (2X - Y)^2,$$

$\frac{X^2 + Y^2}{5}$  is also an integer.

In order to show, how the number  $\eta$  is connected with the other numbers, we remark that

$$\begin{aligned} \{G_1(\gamma) - G_1(\gamma^{-1})\} \{G_2(\gamma) - G_2(\gamma^{-1})\} &= -4p \sin \theta_1 \sin \theta_2 = \\ &= -(t_1 - t_2)(X^2 - XY - Y^2) \end{aligned}$$

and multiplying by

$$2\sqrt{p}(\cos \theta_1 - \cos \theta_2) = (t_1 - t_2) V.$$

we get

$$8p\sqrt{p} \sin \theta_1 \sin \theta_2 (\cos \theta_1 - \cos \theta_2) = \eta = 5V(X^2 - XY - Y^2) = \left\{ \begin{array}{l} \\ = \frac{5V}{4} \{ (2X - Y)^2 - 5Y^2 \} \end{array} \right\} \quad (19)$$

and so it is evident that  $\frac{\eta}{25V}$  is an integer.

An useful relation follows from the identity

$$5(X^2 + Y)^2 - (X^2 + 4XY - Y^2)^2 = 4(X^2 - XY - Y^2)^2.$$

In fact, it shows that the three integers  $\frac{X^2 + Y^2}{5}$ ,  $\frac{S_1V}{5}$  and  $\frac{\eta}{25V}$  are connected by the equation

$$5\left(\frac{X^2 + Y^2}{5}\right)^2 - \left(\frac{S_1V}{5}\right)^2 = 4\left(\frac{\eta}{25V}\right)^2 \dots \dots \dots (20)$$

We must now pay attention to some results of LEGENDRE <sup>1)</sup> concerning the numbers of the form (16)

$$-S_1V = X^2 + 4XY - Y^2 = (X + 2Y)^2 - 5Y^2 = 5X^2 - (2X - Y)^2.$$

The prime factors occurring in such a number can be arranged in two separate classes. The first class contains, besides a possible prime factor 5, only prime factors of the form  $10x \pm 1$ ; all factors of this class may occur raised to any power. In the second class we may find the factor 2 and possibly certain odd prime factors  $q$  different from 5 and not of the form  $10x \pm 1$ . Their exponents necessarily are even. Hence we will have in general

$$-S_1V = X^2 + 4XY - Y^2 = 4^a 5^b H^2(10y \pm 1),$$

where the odd integer  $H$  is a product of prime numbers  $q$ , and  $10y \pm 1$  the product of the prime numbers  $10x \pm 1$ . Moreover, we must observe that whenever a certain factor  $q$  occurs in  $-S_1V$  both numbers  $X$  and  $Y$  must have this factor in common. A single factor 4 will be found in  $-S_1V$ , when  $X$  and  $Y$  are both odd, and only when both numbers are even the exponent  $a$  can exceed unity.

It will appear from (17) that  $S_1$  and  $V$  cannot have a common factor  $q$  and as we have  $V \equiv 0, S_1 \equiv 1 \pmod{5}$ , we must conclude that

$$S_1 = 4^{a_1} H_1^2 (10y_1 \pm 1),$$

$$V = 4^{a_2} 5^b H_2^2 (10y_2 \pm 1),$$

where  $H_1$  and  $H_2$  are prime to each other. It is possible to prove that the exponents  $a_1$  and  $a_2$  cannot be both greater than unity, it being clear besides that the supposition  $a_1 = 0$  involves  $a_2 = 0$  and inversely.

<sup>1)</sup> Essai sur la théorie des nombres, Table III.

3. The preceding considerations concerning the integers  $S_1, S_2, V, \eta, X$  and  $Y$  enable us to ascertain their values and to calculate the coefficients of the equation of the periods for a given prime number  $p = 10w + 1$ , as I now will proceed to show. Let the prime number be  $p = 1091$ , then we begin with examining the possible values of  $S_1$ . From (18) we have

$$S_1 \equiv -9 \pmod{25}$$

and from (10)

$$|S_1| < 133;$$

therefore we must consider as possible values the numbers

$$-109, -84, -59, -34, -9, +16, +41, +66, +91, +116.$$

But any factor  $q$  and also the factor 2 occurring in  $S_1$  must have an even exponent, and so we are led to discard the numbers  $-84, -34, +66, +91$ . For each of the remaining possible values of  $S_1$  we examine the corresponding possible values of  $V$ . According to (13) and to (15) we have

$$\left| \frac{V}{5} \right| < 12 \quad , \quad \left| \frac{S_1 V}{5} \right| < 390,$$

and remembering that  $S_1$  and  $V$  are both odd or both even, that they have no common factor  $q$ , and that a possible factor  $q$  in  $V$  and also the factor 2 always is raised to an even power, we evidently have to retain only the suppositions written down in the following scheme, that also indicates the corresponding values of  $\frac{X^2 + Y^2}{5}$ , as given by (17).

$S_1$	$\left  \frac{V}{5} \right $	$\frac{X^2 + Y^2}{5}$
- 109	1	109
- 59	1, 5	277, 217
- 9	1, 5, 11	345, 285, 45
+ 16	4	304
+ 41	1, 5, 9	313, 253, 113

Examining the values found for  $\frac{X^2 + Y^2}{5}$ , we eliminate again several suppositions by observing that  $\frac{X^2 + Y^2}{5}$  cannot contain a prime factor of the form  $4n - 1$  with an odd exponent. Hence the numbers

$$217 = 7 \times 31, \quad 345 = 3 \times 5 \times 23, \quad 285 = 5 \times 3 \times 19,$$

$$304 = 2^4 \times 19, \quad 253 = 11 \times 23$$

are impossible as values of  $\frac{X^2 + Y^2}{5}$ , so that only five suppositions are left. These are tried by means of the equation (20)

$$5\left(\frac{X^2 + Y^2}{5}\right)^2 - \left(\frac{S_1 V}{5}\right)^2 = 4\left(\frac{\eta}{25V}\right)^2$$

and we find that only two of them lead to a perfect square as value of  $\left(\frac{\eta}{25V}\right)^2$ . Hence we have only to consider the following suppositions

$S_1$	$ V $	$\frac{X^2 + Y^2}{5}$	$4\left(\frac{\eta}{25V}\right)^2$
- 109	1	109	4.109 <sup>2</sup>
- 9	11	45	4. 9 <sup>2</sup>

and the evaluation of the positive or negative integers  $X$  and  $Y$  will enable us to decide between these two.

The first supposition leads to

$$\begin{aligned} X^2 + Y^2 &= 545, \\ X^2 + 4XY - Y^2 &= \pm 545. \end{aligned}$$

Whatever sign we adopt in the second equation, there are no integer values of  $X$  and  $Y$  satisfying both equations and the first supposition is therefore to be rejected.

The second supposition leads to

$$\begin{aligned} X^2 + Y^2 &= 225, \\ X^2 + 4XY - Y^2 &= \pm 495. \end{aligned}$$

From these equations integer values for  $X$  and  $Y$  can be found. Omitting not integer solutions, we find

$$V = +55 \begin{cases} X = \pm 12, \\ Y = \pm 9. \end{cases} \quad \text{or} \quad V = -55 \begin{cases} X = \pm 9, \\ Y = \mp 12, \end{cases}$$

but whatever system of solutions we make use of, we get from (14) and (19)

$$S_1 = -9, \quad S_2 = -3761, \quad \eta = -125.99.$$

Hence the second supposition is to be retained, and the required quintic equation of the periods (11) becomes

$$0 = y^5 + y^4 - 436 y^3 + 131 y^2 + 42453 y - 3015 \quad \dots \quad (21)$$

At the same time we are now able to give the complete algebraic solution of this equation. From (12) we have

$$9 = Q_1 + Q_2 + Q_3 + Q_4$$

and this equation is to be combined with

$$\left\{ \begin{array}{l} + 55 = Q_1 + Q_4 - Q_2 - Q_3, \\ \pm 12 = Q_1 - Q_4, \\ \pm 9 = Q_2 - Q_3, \end{array} \right. \quad \text{or with} \quad \left\{ \begin{array}{l} - 55 = Q_1 + Q_4 - Q_2 - Q_3, \\ \pm 9 = Q_1 - Q_4, \\ \mp 12 = Q_2 - Q_3, \end{array} \right.$$

In this way we find four systems of integer values for the numbers  $Q_1, Q_2, Q_3$  and  $Q_4$ , corresponding with the four sums  $G_1(\gamma), G_1(\gamma^2), G_1(\gamma^3)$  and  $G_1(\gamma^4)$ . In one of these sums for example in  $G_1(\gamma^4)$ , the numbers  $Q_1 + Q_4 - Q_2 - Q_3$  and  $Q_1 - Q_4$  will be positive. Selecting this sum, we will find

$$Q_1 = 22, \quad Q_2 = -7, \quad Q_3 = -16, \quad Q_4 = 10$$

and may then write

$$G_1(\gamma^k) = 22\gamma - 7\gamma^2 - 16\gamma^3 + 10\gamma^4,$$

where  $k$  is one of the numbers 1, 2, 3 or 4. Now  $\gamma^k$  as well as  $\gamma$  itself is a root of (9), therefore we can solve equation (21) by putting

$$f(a, \gamma^k)^5 = 1091 G_1(\gamma^k)^2 G_1(\gamma^{2k}),$$

and then by writing

$$5y + 1 = f(a, \gamma^k) + \frac{1091}{f(a, \gamma^k)} + \frac{f(a, \gamma^k)^2}{G_1(\gamma^k)} + \frac{1091 G_1(\gamma^k)}{f(a, \gamma^k)^2}.$$

From the method applied to the treatment of the particular case  $p = 1091$  it will be evident that in general a finite number of trials will suffice to ascertain the numerical values of  $S_1, S_2$  and  $\eta$ , to write down the equation of the periods and to arrive at its algebraic solution.

4. In the case  $p = 6w + 1, \nu_1 = 6$  the primitive root  $\gamma$  of (2) is one of the roots of the equation

$$\gamma^2 - \gamma + 1 = 0 \quad \dots \dots \dots (22)$$

and according to the general formulae (5), (7) and (8) we have

$$G_0(\gamma) = -1, \quad G_3(\gamma) = (-1)^w G_2(\gamma), \quad G_4(\gamma) = (-1)^w G_1(\gamma), \quad G_5(\gamma) = (-1)^{w-1} p, \\ f(a, \gamma)^6 = (-1)^w p G_1^2(\gamma) G_2^2(\gamma).$$

$$6y + 1 = f(a, \gamma) + \frac{f(a, \gamma)^2}{G_1(\gamma)} + \frac{f(a, \gamma)^3}{G_1(\gamma) G_2(\gamma)} + \frac{(-1)^w f(a, \gamma)^4}{G_1(\gamma) G_2(\gamma)^2} + \frac{f(a, \gamma)^5}{G_1(\gamma)^2 G_2(\gamma)},$$

or

$$6y + 1 = \left\{ f(a, \gamma) + \frac{(-1)^w p}{f(a, \gamma)} \right\} + \left\{ \frac{f(a, \gamma)^2}{G_1(\gamma)} + \frac{p G_1(\gamma)}{f(a, \gamma)^2} \right\} + i^w \sqrt{-p},$$

the latter equation showing that the six periods all are real when  $w$  is even and that they are complex when  $w$  is odd.

Eliminating  $f(a, \gamma)$  the equation of the periods presents itself in the form

$$i^w \sqrt{p} \left[ 108y^2 + 18y \{ 2 + G_2(\gamma) + G_2(\gamma^{-1}) \} + 3 - p(3 + 2(-1)^w) + \right. \\ \left. + 3(-1)^w p \left\{ \frac{G_1(\gamma)}{G_2(\gamma)} + \frac{G_2(\gamma)}{G_1(\gamma)} \right\} + 3 \{ G_2(\gamma) + G_2(\gamma^{-1}) \} + \right. \\ \left. + \{ G_1(\gamma) G_2(\gamma) + G_1(\gamma^{-1}) G_2(\gamma^{-1}) \} \right] = 216y^3 + 108y^2 + 18y(1-p) + \quad (23) \\ + 1 - 3p + 3(-1)^w p \{ G_2(\gamma) + G_2(\gamma^{-1}) \} - 3p \{ G_1(\gamma) + G_1(\gamma^{-1}) \} - \\ - (-1)^w p \left\{ \frac{G_2^2(\gamma)}{G_1(\gamma)} + \frac{G_2^2(\gamma^{-1})}{G_1(\gamma^{-1})} \right\}$$

and the following considerations lead to the evaluation of the coefficients. Supposing  $k\mu \equiv 0, k(\mu+1) \equiv 0 \pmod{6}$  we have (4)

$$G_\mu(\gamma^k) = \sum_{r_1, r_2} \gamma^{k(r_1 + \mu r_2)} = A + B\gamma,$$

and as  $|G_\mu(\gamma^k)| = \sqrt{p}$ , we get

$$p = A^2 + AB + B^2 = (A + B)^2 - AB = (A - B)^2 + 3AB, \quad (24) \\ 4p = (2A + B)^2 + 3B^2 = (2B + A)^2 + 3A^2,$$

from which equations we infer that the factor  $p$  does not occur in one of the integers  $A, B, A + B, A - B, 2A + B$  and  $2B + A$ . Likewise we observe that in the equations

$$(A + B\gamma)^2 = (A^2 - B^2) + \gamma B(2A + B) = U_2 + V_2\gamma, \\ p^2 = U_2^2 + U_2V_2 + V_2^2$$

the integers  $U_2$  and  $V_2$  in this respect are similar to  $A$  and  $B$  and that, if we write

$$(A + B\gamma)^4 = U_4 + V_4\gamma,$$

again neither  $U_4$  nor  $V_4$  is a multiple of  $p$ . Now on the ellipse

$$p = x^2 + xy + y^2$$

there always lie twelve points both coordinates of which are integers, and by a finite number of trials their coordinates can be found. Selecting one of these points with the coordinates  $A, B$ , we may assert that, always in the supposition  $k\mu \equiv 0, k(\mu+1) \equiv 0 \pmod{6}$ , any sum  $G_\mu(\gamma^k)$  can be written in the form  $\beta^h(A + B\beta)$ , where  $\beta$  is either  $\gamma$  or  $\gamma^{-1}$ , if we only give the right value to the exponent  $h$ . So for instance we have

$$G_1(\gamma^2) = \beta^h(A + B\beta), \quad G_1(\gamma) = \beta_1^{h_1}(A + B\beta_1), \quad G_2(\gamma) = \beta_2^{h_2}(A + B\beta_2)$$

and we must prove that  $\beta, \beta_1$  and  $\beta_2$  represent one and the same root of (22). For this purpose we consider the equation

$$G_1(\gamma) G_1(\gamma^2) = (-1)^w G_2(\gamma)^2, \quad \dots \dots \dots (25)$$

immediately derived from (6), which we write in the form

$$\beta_1^{h_1} \beta^h (A + B\beta_1)(A + B\beta) = (-1)^w \beta_2^{2h_2} (A + B\beta_2)^2.$$

The supposition that  $\beta_1$  and  $\beta$  were different roots of equation (22) would lead to

$$\beta_2^2 p = (A + B\beta_2)^2 = U_2 + V_2\beta$$

and that is impossible since neither  $U_2$  nor  $V_2$  has the factor  $p$ . Further,  $\beta_1$  and  $\beta$  being equal, they cannot differ from  $\beta_2$  because in that case we would arrive at

$$\beta^{h+h_1} (A + B\beta)^2 = (-1)^w \beta_2^{2h} (A + B\beta_2)^2,$$

$$\beta_2^2 p^2 = (A + B\beta_2)^4 = U_4 + V_4\beta_2,$$

and again that would be impossible.

In the first place I proceed to the evaluation of  $h$  by deducing the equation of the periods of order  $\frac{p-1}{3}$ . Remembering that  $\gamma$  still denotes one of the roots of (22), we have according to (5), (7) and (8)

$$G_0(\gamma^2) = -1, \quad G_2(\gamma^2) = -p$$

$$f(a, \gamma^2)^3 = p G_1(\gamma^2)$$

$$3y + 1 = f(a, \gamma^2) + \frac{f(a, \gamma^2)^2}{G_1(\gamma^2)} = f(a, \gamma^2) + \frac{p}{f(a, \gamma^2)}$$

and eliminating  $f(a, \gamma^2)$  the required equation becomes

$$y^3 + y^2 + \frac{1}{3} y (1-p) + \frac{1}{27} \left[ 1 - 3p - p \{ G_1(\gamma^2) + G_1(\gamma^{-2}) \} \right] = 0. \quad (26)$$

Here the last coefficient is an integer, hence we have

$$1 - 3p - p \{ G_1(\gamma^2) + G_1(\gamma^{-2}) \} \equiv 0 \pmod{27} \dots (27)$$

and this congruency will give the value of  $h$  as soon as  $p$  is a known prime number. In fact, we may write

$$\beta^h = L + M\beta$$

and the corresponding values of  $h$ ,  $L$  and  $M$  must be those of the following scheme

$h$	$L$	$M$
0	+ 1	0
1	0	+ 1
2	- 1	+ 1
3	- 1	0
4	0	- 1
5	+ 1	- 1.

In this way we get

$$G_1(\gamma^2) + G_1(\gamma^{-2}) = L(2A + B) + M(A - B)$$

and then from (27) the congruency

$$1 - 3p - pL(2A + B) - pM(A - B) \equiv 0, \quad (\text{mod } 27)$$

by which the exponent  $h$  is readily determined. A second congruency will determine the exponent  $h_2$ . In fact, the equation of the periods of order  $\frac{p-1}{6}$  (23), when rationalised, must have integer coefficients, and that requires

$$2 + G_2(\gamma) + G_2(\gamma^{-1}) \equiv 0 \quad (\text{mod } 6), \dots \dots \dots (28)$$

or

$$2 + L(2A + B) + M(A - B) \equiv 0. \quad (\text{mod } 6)$$

This congruency in connexion with the preceding scheme will give the value of  $h_2$  and finally  $h_1$  is found from the congruency

$$h_1 + h \equiv 3w + 2h_2 \quad (\text{mod } 6) \dots \dots \dots (29)$$

directly derived from (25).

Now all the coefficients of (23) are known, and we have only to rationalise this equation, to obtain the equation of the periods of order  $\frac{p-1}{6}$ .

5. As an example I will treat the case  $p = 1063$ . Equation (24) becomes

$$(2A + B)^2 = 4252 - 3B^2,$$

and after a few trials we find  $\pm 3, \pm 31$  and  $\pm 34$  as possible values of  $B$ . Giving, for instance,  $B$  the value 34 and adopting  $-3$  as one of the two corresponding values of  $A$ , we may write

$$G_1(\gamma^2) = \beta^h (-3 + 34\beta).$$

Hence the congruency (27) becomes

$$-2 - 10L - 8M \equiv 0 \quad (\text{mod } 27)$$

and considering the scheme, we find that we have necessarily  $L = -1, M = +1, h = 2$ . Having thus established the equation

$$G_1(\gamma^2) = \beta^2 (-3 + 34\beta),$$

we have also the result

$$G_1(\gamma^2) + G_1(\gamma^{-2}) = -65,$$

and by the way we have found that the equation (26) of the periods of order  $\frac{p-1}{3}$  is

$$y^3 + y^2 - 354y + 2441 = 0.$$

The congruency (28) now takes the form

$$2 + 28L - 37M \equiv 0 \pmod{6},$$

and we necessarily have  $L = 1$ ,  $M = 0$ ,  $h_2 = 0$ ,

$$G_2(\gamma) = (-3 + 34\beta).$$

Hence from (29) we get  $h_1 = 1$

$$G_1(\gamma) = \beta(-3 + 34\beta)$$

and then successively

$$G_1(\gamma) + G_1(\gamma^{-1}) = -37, \quad G_2(\gamma) + G_2(\gamma^{-1}) = 28,$$

$$\frac{G_1(\gamma)}{G_2(\gamma)} + \frac{G_1(\gamma^{-1})}{G_2(\gamma^{-1})} = 1, \quad G_1(\gamma)G_2(\gamma) + G_1(\gamma^{-1})G_2(\gamma^{-1}) = -2099,$$

$$\frac{G_2^2(\gamma)}{G_1(\gamma)} + \frac{G_2^2(\gamma^{-1})}{G_1(\gamma^{-1})} = 65.$$

Substituting these results in (23) we obtain

$$i\sqrt{1063} \left( \frac{1}{2}y^2 + \frac{5}{2}y - 29 \right) = \left( y^3 + \frac{1}{2}y^2 - \frac{177}{2}y + 438 \right)$$

and then by squaring we find

$$0 = y^6 + y^5 + 89y^4 + 3445y^3 - 15913y^2 - 231661y + 1085827$$

as the equation of the periods of order  $\frac{p-1}{6}$ , an equation all roots of which are complex. Solving algebraically, we have at once

$$f(a, \gamma)^6 = -1063\beta^2(-3 + 34\beta)^4 = -1063\beta^2R^4,$$

$$6y + 1 = f(a, \gamma) - \frac{1063}{f(a, \gamma)} + \frac{f^2(a, \gamma)}{\beta R} + \frac{1063\beta R}{f^2(a, \gamma)} + \frac{f^3(a, \gamma)}{\beta R^2}.$$

It will be found that the equation of the periods of order  $\frac{p-1}{4}$  may be derived in a quite similar way.

**Chemistry.** — “Equilibria in systems, in which phases, separated by a semi-permeable membrane” IX. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of May 30, 1925).

*Two ternary systems.*

We take an osmotic equilibrium:

$$E = E_1 \mid E_2$$

in which the separate parts  $E_1$  and  $E_2$  are both ternary systems. Of course they have always one component in common, viz. the diffusing substance  $W$  (water); both the other components can be either the same or different. Consequently we distinguish three cases:

1. There are three common components; then each of the separate systems contains f.i. the substances  $W + X + Y$ .

2. There are only two common components; then the one system contains f.i. the substances  $W + X + Y$  and the other system the substances  $W + X + Z$ .

3. There is only one common component, viz. the diffusing substance  $W$ . Then the one system contains f.i. the substances  $W + X + Y$  and the other system the substances  $W + Z + U$ .

In previous communications we have discussed already several examples of the first case; now we shall consider some examples of the other cases.

*Both the systems contain two common components.*

We represent the phases of the system  $E_1$ , which contains the components  $W + X + Y$  by points of a triangle  $WXY$ ; those of a system  $E_2$ , which contains the components  $W + X + Z$  by points of a triangle  $WXZ$ . In fig. 1 both triangles are placed against one another with the side  $WX$ , they are united in a single diagram.

It appears from the figure that we have assumed that in the system  $W + X + Y$  both the components  $X$  and  $Y$  occur as solid phases; in the system  $W + X + Z$ , however, only the solid substance  $X$ . The saturation-curves of those systems are represented by the curves  $ab$ ,  $db$  and  $dg$ . In accordance with the previous the arrows indicate the direction in which the O.W.A. of the saturated liquids increases.

We consider, just as formerly, the osmotic equilibrium:

$$E = E_1 \mid E_2 \dots \dots \dots (1)$$

again at constant temperature and under constant pressure; we assume again that the pressure  $P_1$  of system  $E_1$  is equal to the pressure  $P_2$  of system  $E_2$ . Then follows from the membrane-phase-rule (Comm. VII):

$$\text{number of freedoms} = 3 + 3 - (r_1 + r_2) - 1 = 5 - (r_1 + r_2) \quad (2)$$

in which  $r_1$  indicates the number of phases of  $E_1$  and  $r_2$  that of  $E_2$ .

In the osmotic equilibrium:

$$E = L_1 \mid L_2 \dots \dots \dots (3)$$

$L_1$  and  $L_2$  represent two liquids. If we take a binary liquid  $L_q$ , represented by point  $q$  of the side  $WX$ , then all liquids of the system  $W + X + Y$ , which are isotonic with  $L_q$  are represented by points of the isotonic curve  $qq_1$ ; all liquids of the system  $W + X + Z$  by an isotonic curve  $qq_2$ .

Consequently the two isotonic curves  $qq_1$  and  $qq_2$  start from point  $q$ ; the one is situated in triangle  $WXY$ , the other in triangle  $WXZ$ . Each liquid of curve  $qq_1$ , therefore, is not only isotonic with each other liquid of this curve, but also with all liquids of curve  $qq_2$ .

Generally, therefore, with each liquid, which contains the components  $W + X + Y$  is isotonic not only a series of liquids with the same components, but also a series of liquids with the components  $W + X + Z$ .

Consequently two isotonic curves start from each point of the side  $WX$ ; we call them conjugated isotonic curves; some of them are dotted in fig. 1. Liquid  $r_1$  is isotonic, therefore, with the liquids  $L_t, L_d, L_v$  and  $L_{r_2}$ ; liquid  $a$  with the liquids  $L_c, L_e, L_o$  and  $L_h$ ; etc. The binary  $W + Y$ -containing liquid  $r_1$  is isotonic, therefore, with the binary  $W + Z$ -containing liquid  $r^2$ ; etc.

Also follows from the above considerations that the osmotic equilibrium (3) has three freedoms. If we take f.i. for  $L_1$  a definite liquid, f.i.  $L_t$ , then two freedoms disappear, consequently  $L_2$  has left still one freedom; it is represented by a point of the conjugated isotonic curves  $dr_1$  and  $dr_2$ . We are able to represent this (compare f. i. previous communications) by:

$$E = L_t \mid L(1 - dr_1 - dr_2) \dots \dots \dots (4)$$

from which it appears that the liquid  $L$  has one freedom and is represented by a point of the conjugated curves  $dr_1$  and  $dr_2$ .

If we represent the thermodynamical potential and the composition of liquid  $L_1$  by

$$\zeta_1 \text{ and } x_1X + y_1Y + (1 - x_1 - y_1)W \dots \dots \dots (4a)$$

and those of  $L_2$  by:

$$\zeta_2 \text{ and } x_2X + z_2Z + (1 - x_2 - z_2)W \dots \dots \dots (4b)$$

then is valid for equilibrium (3) the equation:

$$\zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} = \zeta_2 - x_2 \frac{\partial \zeta_2}{\partial x_2} - z_2 \frac{\partial \zeta_2}{\partial z_2} \dots \dots \dots (5)$$

As in (5) four variables occur, it also follows from this that the osmotic equilibrium (3) has three freedoms. This also follows at once from (2), if we put herein  $r_1 = 1$  and  $r_2 = 1$ .

If we bring in osmotic contact the liquids  $L_s$  and  $L_u$  (fig. 1) then, as the O.W.A. of  $L_u$  is larger than that of  $L_s$ , water shall diffuse from  $L_s$  towards  $L_u$ . Therefore, liquid  $L_s$  moves along the straight line  $Ws$ , away from point  $W$ , liquid  $L_u$  along the straight line  $uW$  towards  $W$ . This diffusion continues till both liquids have got the same O.W.A., therefore, till both come on conjugated isotonic curves. When this is f. i. the case on the curves  $dr_1$  and  $dr_2$ , then is formed the osmotic equilibrium:

$$E = L_s \mid L_u \dots \dots \dots (6)$$

As we shall deduce further, it depends not only on the composition, but also on the ratio of the quantities of the original liquids  $L_s$  and  $L_u$ , on which isotonic curves they will get the same O.W.A.

In order to show this, we take  $n_1$  quantities of  $L_s$  with the composition (4<sup>a</sup>) and  $n_2$  quantities of  $L_u$  with the composition (4<sup>b</sup>).

We assume that from this arise,  $n'_1$  quantities of a liquid  $L_s'$  with the composition:

$$x'_1 X + y'_1 Y + (1 - x'_1 - y'_1) W$$

and  $n'_2$  quantities of  $L_u'$  with the composition:

$$x'_2 X + z'_2 Z + (1 - x'_2 - z'_2) W.$$

If we express that the total quantity of the diffusing substance  $W$  remains constant and that also the quantity of each of the not-diffusing substances  $X$ ,  $Y$  and  $Z$  remains constant on each of the sides of the membrane, then we find the equations:

$$\left. \begin{aligned} n'_1 + n'_2 &= n_1 + n_2 \\ n'_1 x'_1 &= n_1 x_1 & n'_1 y'_1 &= n_1 y_1 & n'_2 x'_2 &= n_2 x_2 & n'_2 z'_2 &= n_2 z_2 \end{aligned} \right\} (7)$$

From this follows by elimination of  $n'_1$  and  $n'_2$ :

$$\frac{x'_1}{y'_1} = \frac{x_1}{y_1} \quad \frac{x'_2}{z'_2} = \frac{x_2}{z_2} \quad 1 + \frac{n_2}{n_1} = \frac{x_1}{x'_1} + \frac{n_2}{n_1} \cdot \frac{x_2}{x'_2} \dots \dots \dots (8)$$

The first one of those equations expresses that the liquid  $L_s'$  proceeds along the line  $Ws$ , the second one expresses that the liquid  $L_u'$  proceeds



systems which form together a quaternary system. The liquids under consideration are situated in two of the four triangles, which limit the tetrahedron  $WXYZ$ , which should represent in space this quaternary equilibrium. Consequently the complex  $k$  is situated really in space within the tetrahedron and not in the plane of fig. 1, which represents only two side-planes of the tetrahedron, drawn in a same plane.

If, however, we consider fig. 1 as a perspective projection of the tetrahedron  $WXYZ$ , then follows from this at once the property above mentioned; we are able to deduce this still also in the following way.

From fig. 1 viz. follows that we may put:

$$Ws = ax_1 \quad Ws' = ax'_1 \quad Wu = \beta x_2 \quad Wu' = \beta x'_2 \quad , \quad (10)$$

in which  $a$  and  $\beta$  have definite values. If we take the line  $Wu$  as  $X$ -axis and the line  $Wt$  as  $Y$ -axis of a system of coördinates, then is:

$$\frac{X}{\beta x_2} + \frac{Y}{ax_1} = 1 \quad \text{the equation of the line } su$$

$$\frac{X}{\beta x'_2} + \frac{Y}{ax'_1} = 1 \quad \text{" " " " " } s'u'$$

Calculating from this the  $X$  or the  $Y$  of the point of intersection  $k$  of those two lines, then we easily find:

$$sK : uK = \left( \frac{x_1}{x'_1} - 1 \right) : \left( 1 - \frac{x_2}{x'_2} \right) . . . . . (11)$$

With the aid of (7) we find from this the equation (9) so that the property above mentioned is proved.

In fig. 1, therefore,  $k$  shall be the point of intersection of the lines  $su$  and  $tv$ ; the liquids  $s'$  and  $u'$ , which occur during the diffusion, are situated, therefore, in such a way that the line  $s'u'$  goes through the point  $k$ .

We now consider the osmotic system:

$$X + L_d \left| L . . . . . (12) \right.$$

of fig 1. As  $L_d$  is the liquid, which is formed when the solid substance  $X$  takes a little water in,  $L_d$  has the same O.W.A. as the solid substance  $X$ . In a similar way and with the same way of representation as previously (compare f.i. Comm. VII) we find:

$$E = X + L_d \left| L(1 - dr_1 - dr_2) . . . . . (13) \right.$$

$$X \leftarrow L(2 - Wdr_1 - Wdr_2) . . . . . (14)$$

$$X \left| L(2 - dr_1 YX - dr_2 ZX) . . . . . (15) \right.$$

Limiting ourselves to stable liquids (viz. only to the unsaturated and saturated liquids, excluding the supersaturated liquids) then (15) passes into:

$$X \mid L(2 - dr_1 ab - dr_2 Zg) \dots \dots \dots (16)$$

(13) indicates that the liquid  $L$ , which is isotonic with the liquid  $L_d$ , has one freedom and is represented by points of the curves  $dr_1$  and  $dr_2$ .

(14) means that the liquids from which water diffuses towards the solid substance  $X$ , have two freedoms and are represented by points of the regions  $Wdr_1$  and  $Wdr_2$ .

(16) means that the liquids, which can be in osmotic contact with the solid substance  $X$ , without anything happening, have two freedoms and are represented by points of the region  $dr_1 ab$  or  $dr_2 Zg$ .

We may express this also in the following way:

the O.W.A. of the solid substance  $X$  is equal to that of the liquids of curves  $dr_1$  and  $dr_2$ , larger than that of the liquids of the regions  $Wdr_1$  and  $Wdr_2$  and smaller than that of the liquids of the regions  $dr_1 ab$  and  $dr_2 Zg$ .

Let us take now the osmotic system:

$$Y + L_a \mid L \dots \dots \dots (17)$$

in which  $L_a$  (fig. 1) is the liquid, which arises, when the solid substance  $Y$  takes a little of the diffusing substance  $W$ . We now find:

$$E = Y + L_a \mid L(1 - ac - eh) \dots \dots \dots (18)$$

$$Y \leftarrow L(2 - Wdca - Wdeh) \dots \dots \dots (19)$$

$$Y \mid L(2 - acb - eh Zg) \dots \dots \dots (20)$$

This means: the O.W.A. of the solid substance  $Y$  is equal to that of the liquids of curves  $ac$  and  $eh$ , larger than that of the liquids of the regions  $Wdca$  and  $Wdeh$  and smaller than that of the liquids of the regions  $acb$  and  $eh Zg$ .

Consequently here a series of liquids exists, which do not contain the substance  $Y$  (viz. of curve  $eh$ ) and yet they have the same O.W.A. as the solid substance  $Y$ . Also there are now two liquids, saturated with the solid substance  $X$ , which have also the same O.W.A. as the solid substance  $Y$ . One of them (viz. liquid  $c$ ) contains the substance  $Y$ , the other one (viz. liquid  $e$ ), however, does not contain the substance  $Y$ .

In the osmotic system:

$$X + Y + L_b \mid L \dots \dots \dots (21)$$

$L_b$  is the liquid which arises, when solid  $X + Y$  takes a little water in. Limiting ourselves again to stable states, then we find:

$$E = X + Y + L_b \left\{ L(1-fi) \dots \dots \dots (22) \right.$$

$$X + Y \left\arrowleft L(2 - Wdba - Wdfi) \dots \dots (23) \right.$$

$$X + Y \left\{ L(2 - fiZg) \dots \dots \dots (24) \right.$$

Consequently there is only one liquid, containing  $X + Y$ , viz.  $L_b$ , which has the same O.W.A. as the solid mixture  $X + Y$ ; indeed there is still a series of liquids, viz. those of curve  $fi$ , which also have this same O.W.A. but those liquids do not contain the substance  $Y$ .

Also we find in the system  $W + X + Y$  no liquids with a greater O.W.A. than those of the solid mixture  $X + Y$ ; we find them in the region  $fiZg$  of the system  $W + X + Z$ .

If we bring in osmotic contact  $L_c$  and  $L_u$  then nothing happens; both liquids are situated viz. on conjugated isotonic curves and have, therefore, the same O.W.A.

If we bring in osmotic contact  $L_c$  and  $L_v$  then, as the O.W.A. of  $L_c$  is greater than that of  $L_v$ , the inversion:

$$L_c \leftarrow L_v$$

shall occur; the saturated liquid  $L_c$  shall become unsaturated, therefore.

If we bring in osmotic contact  $L_c$  and  $L_w$ , then water shall diffuse from  $L_c$  towards  $L_w$ ; consequently we have:

$$L_c \rightarrow L_w.$$

Consequently  $L_c$  shall pass into a liquid between  $c$  and  $b$ , with separation of the solid substance  $X$ .

If we bring in osmotic contact solid  $X + Y$  with  $L_v$ , then, as the O.W.A. of the solid  $X + Y$  is greater than that of liquid  $L_v$ , water shall diffuse from the liquid towards  $X + Y$ . Consequently we get the inversion:

$$X + Y \leftarrow L_v.$$

When a sufficient quantity of  $X + Y$  is present, then at last is formed the osmotic equilibrium:

$$E = X + Y + L_b \left\{ L_w.$$

*Both the systems contain one common component only.*

We now take the osmotic equilibrium:

$$E = E_1 \mid E_2$$

in which the separate parts have only the diffusing substance  $W$  in common. We shall represent the phases of  $E_1$  with the components  $W + X + Y$  by points of triangle  $WXY$  (fig. 2); those of system  $E_2$  with the components  $W + Z + U$  by points of triangle  $WZU$  (fig. 3).

We assume, as is apparent from those two diagrams, that in the one system the components  $X$  and  $Y$  occur as solid phases, in the other system the component  $U$ . The arrows on the saturation-curves  $ci$ ,  $hi$  and  $em$  indicate the direction in which the O.W.A. of the saturated solutions increases.

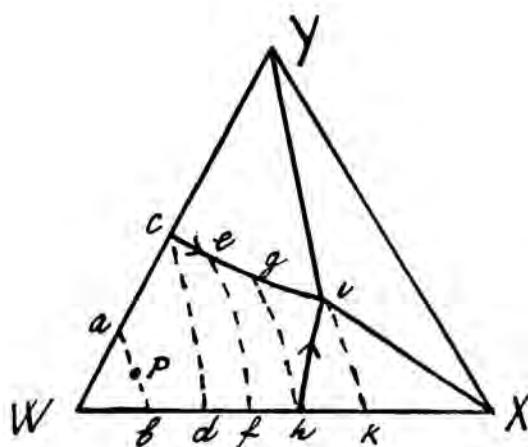


Fig. 2.

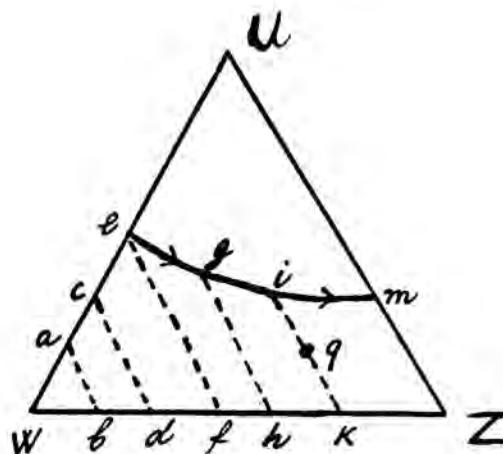


Fig. 3.

We now draw in fig. 2 an isotonic curve  $ab$ ; now we are able to draw also in fig. 3 an isotonic curve  $ab$ , the liquids of which have the same O.W.A. as the liquids of curve  $ab$  in fig. 2. The curves  $ab$  of figs. 2 and 3, which we shall call for the sake of distinction  $(ab)_2$  and  $(ab)_3$  are, therefore, conjugated isotonic curves.

We now assume that the dotted curves, which are indicated in both figures by the same letters, represent also conjugated isotonic curves; f.i.  $(cd)_2$  and  $(cd)_3$ ;  $(ef)_2$  and  $(ef)_3$ ; etc.

For the osmotic equilibrium:

$$E = L_2 \mid L_3$$

in which  $L_2$  represents a liquid of fig. 2 and  $L_3$  a liquid of fig. 3, is true the equation for equilibrium:

$$\zeta_2 - x \frac{\partial \zeta_2}{\partial x} - y \frac{\partial \zeta_2}{\partial y} = \zeta_3 - z \frac{\partial \zeta_3}{\partial z} - u \frac{\partial \zeta_3}{\partial u} \dots (25)$$

in which  $\zeta_2$  and  $\zeta_3$  represent the thermodynamical potentials of the liquids  $L_2$  and  $L_3$ .

We now bring in osmotic contact liquid  $L_p$  [on curve  $(a b)_2$ ] with liquid  $L_q$  [on curve  $(i k)_3$ ]. As the O.W.A. of  $L_q$  is greater than that of  $L_p$ , water shall diffuse from  $L_p$  towards  $L_q$ . Consequently  $L_q$  moves along the line  $Wq$  starting from  $q$  towards  $W$ ;  $L_p$  shifts along the line  $Wp$  further away from  $p$ . For this diffusion, which continues till both liquids reach conjugated isotonic curves, the same is true as is deduced above for fig. 1.

In the osmotic system:

$$Y + L(c)_2 \left| L \right.$$

$L(c)_2$  (fig. 2) is the liquid, which arises when a little water diffuses towards the solid substance  $Y$ . Limiting ourselves again to stable states, then follows:

$$E = Y + L(c)_2 \left| L [1 - (cd)_2 - (cd)_3] \right.$$

$$Y \leftarrow L [2 - (Wcd)_2 - (Wcd)_3] \left| L \right.$$

$$Y \left| L [2 - (cdhi)_2 - (cdZme)_3] \right.$$

This means: the O.W.A. of the solid substance  $Y$  is equal to that of the liquids of curve  $cd$  in figs. 2 and 3; greater than that of the liquids of the region  $Wcd$  in figs. 2 and 3; smaller than that of the liquids of the region  $cdhi$  in fig. 2 and of the region  $cdZme$  in fig. 3.

If we bring in osmotic contact the solid substance  $Y$  with liquid  $q$  (which contains the components  $W + U + Z$ ) then nothing happens, therefore; if, however, we bring in osmotic contact solid  $Y$  with a liquid of curve  $(a b)_3$  [which contains, therefore, also the components  $W + U + Z$ ] then  $Y$  shall flow away totally or partly.

In the osmotic system:

$$X + L(h)_2 \left| L \right.$$

$L(h)_2$  (fig. 2) is the liquid which arises when the solid substance  $X$  takes a little water in.

We find from this:

$$E = X + L(h)_2 \left| L [1 - (hg)_2 - (hg)_3] \right.$$

$$X \leftarrow L [2 - (Whgc)_2 - (Whge)_3] \left| L \right.$$

$$X \left| L [2 - (hgi)_2 - (hgmZ)_3] \right.$$

From this appears a.o. that from all liquids of the region  $Whgc$  in fig. 2 (consequently with the components  $W+X+Y$ ) and from all liquids of the region  $Whge$  in fig. 3 (consequently with the components  $W+Z+U$ ) water will diffuse towards the solid substance  $X$ ; the other liquids let  $X$  unchanged.

In similar way the reader may find also the liquids, which have either the same or smaller or greater O.W.A. than the solid substance  $U$  or the solid mixture  $X+Y$ .

If we bring in osmotic contact the solid substances  $X$ ,  $Y$  or  $U$  or the solid mixture  $X+Y$  with a liquid  $L$ , which contains the components  $W+X+Y$  (fig. 2) or the components  $W+Z+U$  (fig. 3) then we may distinguish several cases.

1.  $L$  is situated within the region  $Wcd$  of fig. 2 or 3.  
 $X$ ,  $Y$ ,  $U$  and  $X+Y$  flow away totally or partly.
2.  $L$  is situated within the region  $cdfe$  of fig. 2 or 3.  
 $X$ ,  $U$  and  $X+Y$  flow away totally or partly;  $Y$  remains unchanged.
3.  $L$  is situated within the region  $efhg$  of fig. 2 or 3.  
 $X$  and  $X+Y$  flow away totally or partly;  $Y$  and  $U$  remain unchanged.
4.  $L$  is situated within the region  $hgi$  of fig. 2 or within the region  $hgik$  of fig. 3.  
 $X+Y$  flows away totally or partly;  $X$ ,  $Y$  and  $U$  remain unchanged.
5.  $L$  is situated within the region  $ikZm$  of fig. 3.  
 $X$ ,  $Y$ ,  $U$  and  $X+Y$  remain unchanged.

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*(To be continued.)*

**Physics.** — “*The characteristics of tungsten and the candle power of the black body*”. By C. ZWIKKER. (Communicated by Prof. P. ZEEMAN).

(Communicated at the meeting of May 30, 1925).

The importance of tungsten for the glowlamp and radio industry, as well as the scientific interest we have in an extensive knowledge of the physical properties of a material, which may be obtained in a very pure state, have lead me to a redetermination of the diverse properties of this metal at high temperatures. The final results have been collected in table I.

The temperature has been measured by an optical pyrometer method, making use of PLANCK's radiation law. The value of  $C_2$  which occurs in this formula is taken as  $14\,330 \mu$  degr. The basispoint used for the temperature scale is the melting point of gold, for which the value of  $1336^\circ$  KELVIN is adopted. The melting point of the sample of gold, used by me, which was kindly supplied to us by Dr. v. HETEREN, was in concordance with the goldpoint of the Physikalisch Technische Reichsanstalt.

The spectral emissivity has been determined by comparing the inner and outer brightness of a tungsten rod in which a hole had been drilled and which was raised to a high temperature by different methods. With this so determined spectral emissivity  $e_\lambda$ , the true temperature  $T$  has been calculated from the observed „brightness temperature”  $S$  by the relation:

$$\frac{1}{T} - \frac{1}{S} = \frac{\lambda 2,303 \log e_\lambda}{C_2}.$$

Electrical measurements have been performed by a compensation method. The standard resistance and the standard element had been verified by the P. T. R. The *resistivity* was obtained from the electrical resistance of a tungsten filament of known dimensions; the *total radiation* from the wattage input of this filament.

Corrections have been made for the cooling at the filament junctions.

The brightness given in the table is the normal candle power, expressed in International Candles. The photometric standard lamps had been standardized by the P. T. R. in 1922. The candle power was given by the P. T. R. in Hefner Candles and was converted by us to International Candles, assuming that:

$$1 \text{ I.C.} = 1,11 \text{ H.C.}$$

TABLE I. The characteristics of tungsten.

Temperature	Spectral emissivity $\lambda = 0.665$	Brightness temperature $\lambda = 0.665$	Colour temperature	Resistivity	Total radiation	Brightness	Thermionic emission	Rate of vaporization	Thermal conductivity	Thomson-effect
$T$	$e_\lambda$	$S_\lambda$	$T_c$	$\rho$	$\eta$	$B$	$i$	$m$	$k$	$\tau$
1200	0.458	1150	1210	30.9	1.70	0.0071				
1300	0.456	1240	1312	34.0	2.70	0.0311				
1400	0.454	1331	1414	37.1	3.94	0.117				
1500	0.451	1421	1517	40.2	5.52	0.370	$0.102 \cdot 10^{-6}$	$1.78 \cdot 10^{-22}$		
1600	0.449	1510	1619	43.4	7.90	1.07	$0.102 \cdot 10^{-5}$	$1.78 \cdot 10^{-20}$		
1700	0.446	1597	1722	46.7	10.7	2.62	$0.812 \cdot 10^{-5}$	$1.02 \cdot 10^{-18}$		
1800	0.444	1685	1825	49.9	14.1	5.75	$0.490 \cdot 10^{-4}$	38.0	1.22	-18
1900	0.442	1773	1929	53.2	18.6	12.3	$0.257 \cdot 10^{-3}$	932	1.26	-20
2000	0.440	1859	2033	56.7	24.0	23.2	$0.112 \cdot 10^{-2}$	$15.5 \cdot 10^{-15}$	1.29	-22
2100	0.438	1945	2137	60.1	30.5	42.4	0.00427	214	1.31	-24
2200	0.435	2028	2242	63.5	38.2	72.0	0.0141	$2.24 \cdot 10^{-12}$	1.33	-26
2300	0.432	2111	2347	66.9	47.2	116.5	0.0437	19.5	1.35	-28
2400	0.430	2193	2452	70.5	57.3	185	0.123	138	1.37	-30
2500	0.427	2275	2557	74.0	69.4	279	0.302	833	1.39	
2600	0.424	2357	2663	77.6	83.5	409	0.776	$4.17 \cdot 10^{-9}$	1.405	
2700	0.422	2437	2770	81.2	100.5	598	1.74	20.4	1.42	
2800	0.420	2517	2878	84.8	119.0	823	3.74	83.3	1.43	
2900	0.417	2596	2986	88.5	139	1110	7.57	309		
3000	0.415	2675	3094	92.3	162	1490	14.9	$1.05 \cdot 10^{-6}$		
3100	0.413	2753	3202	97.0	189	1960	28.1	3.31		
3200	0.411	2829	3311	99.9	221	2530	50.5	10.0		
3300	0.409	2903	3422	103.8	254	3250	87.7	26.3		
3400	0.407	2978	3533	107.8	291	4080	149	70.8		
degr. K		degr. K	degr. K	$\mu\Omega$ cm	Watts $\text{cm}^{-2}$	I.C. $\text{cm}^{-2}$	Amp. $\text{cm}^{-2}$	gr. $\text{cm}^{-2}$ sec. $^{-1}$	Watts $\text{cm}^{-1}$ degr. $^{-1}$	$\mu\text{V} \cdot \text{degr.}^{-1}$

For the purpose of measuring the *thermionic emission* lamps were constructed in which the filament was surrounded by an electrode in the usual manner. A positive charge given to this electrode collected the emitted electrons. The electron emission is given by the formula:

$$i = AT^2 e^{-\frac{b}{T}} \text{ Amp./cm}^2$$

in which

$$A = 60,2$$

$$b = 52230.$$

The rate of vaporization has been determined from the decrease in diameter of a glowing tungsten filament maintained at a constant temperature, as calculated from the increase of its resistance, measured as a function of time. For the rate of vaporization the following formula holds:

$$\log m = 11,92 - \frac{4,84 \cdot 10^4}{T} - 0,368 \log T - 0,00016 T.$$

From the observed temperature variation near the leads, *heat conductivity* determinations were made. The positive and the negative filament end showed a somewhat different temperature variation. This is caused by the *Thomson effect*; the Thomson coefficient can be calculated from the ratio of the temperature gradients at both leads.

The *colour temperature* of tungsten at a temperature  $T$  is defined as

TABLE II. The candle power of the black body

$T$	$B$
1300	0.015
1336	0.111
1400	0.261
1500	0.818
1600	2.26
1700	5.74
1800	12.4
1900	25.7
2000	50.1
2100	91.6
2200	156
2300	256
2400	410
2500	620
2600	915
$\text{ок}$	I.C./cm <sup>2</sup>

the temperature of the black body to obtain the same energy distribution in the visible spectrum as tungsten gives. The colour temperature is of great importance because of the possibility to calculate the candle power of the black body from the relation between brightness temperature, colour temperature and candle power of tungsten by the formula:

$$B_{\text{Black Body at } T_c} = B_{\text{Tungsten at } S} \cdot e^{\frac{C_2}{2.303 \lambda} \left( \frac{1}{S} - \frac{1}{T_c} \right)}$$

Furthermore direct candle power determinations have been done of the black body. In this study the pyrometer bench was used as a micro-photometer, it being standardized for white as well as for red (monochromatic) light. The red and the white brightness of the black body were measured in immediate succession, the red brightness determining the temperature. These measurements extended over the temperature range from 1300 to 2600° K, and were in complete concordance with the brightness measurements of tungsten filaments. Our data on the candle power of the black body are given in table II.

These measurements give for the least mechanical equivalent of light the value:

$$M = 0,00146 \text{ Watts per Intern. Lumen.}$$

*Eindhoven, May 11, 1925.*

*Natuurkundig Laboratorium der  
N.V. PHILIPS' Gloeilampenfabrieken.*

**Mathematics.** — "Intuitionistischer Beweis des Jordanschen Kurvensatzes." By Prof. L. E. J. BROUWER.

(Communicated at the meeting of June 27, 1925.)

§ 1. Unter einer *ebenen Kernspezies* verstehen wir eine Spezies von Punktkernen der Ebene.

Unter einer *geschlossenen stetigen Kurve*  $S$  verstehen wir eine ebene Kernspezies, welche eindeutiges Bild eines mit einem Umlaufsinne versehenen (als Kernspezies zu betrachtenden) Quadratumfangs  $K$  ist.

Nach Bd. XXVII, S. 193 dieser Proceedings ist die geschlossene stetige Kurve  $S$  *gleichmässig stetiges* Bild des Quadratumfangs  $K$ .

Unter einer *Jordanschen Kurve*  $J$  verstehen wir eine geschlossene stetige Kurve, welche als Abbildung des Quadratumfangs  $K$  eine stetige (mithin eindeutige und nach Bd. XIII, Nr. 2, S. 4 der Verhandlungen dieser Akademie auch gleichmässig stetige) Umkehrung besitzt.

Auf Grund der Beziehung zwischen  $J$  und  $K$  existiert zu jedem  $\varepsilon$  ein solches mit  $\varepsilon$  gegen 0 konvergierendes (d.h. positiv-konvergierendes)  $\varepsilon_1$ , dass die Bildpunktkerne  $A'$  und  $B'$  auf  $K$  je zweier Punktkerne  $A$  und  $B$  von  $J$ , deren Entfernung  $< \varepsilon^1$ ) ist, eine Entfernung  $< \varepsilon_1$  besitzen, so dass auch die Breite von einem der Bogen  $A'B'$  von  $K$  kleiner als  $\varepsilon_1$  ist und somit die Breite von einem der Bogen  $AB$  von  $J$  kleiner als  $\varepsilon_2$ , wo  $\varepsilon_2$  mit  $\varepsilon_1$ , also mit  $\varepsilon$ , gegen 0 konvergiert.

Sei nun  $\varepsilon$  so gewählt, dass das zugehörige  $\varepsilon_2 < \frac{1}{3}$  der Breite von  $J$  ist, und seien  $A, B$  und  $C$  drei derartige Punktkerne von  $J$ , dass  $\varrho(A, C) < \frac{1}{2}\varepsilon$  und  $\varrho(C, B) < \frac{1}{2}\varepsilon$ . Alsdann kann man entweder einen  $A, B$  und  $C$  enthaltenden Bogen von  $J$  der Breite  $< \varepsilon_2$  oder für je zwei der Punktkerne  $A, B$  und  $C$  einen Abstand  $> 0$  bestimmen. Im letzteren Falle sei  $A\alpha B$  ein Bogen von  $J$  der Breite  $< \varepsilon_2$ ; zu diesem Bogen muss  $C$  entweder gehören, oder von ihm einen Abstand  $> 0$  besitzen. Im ersteren Falle hat man wiederum einen  $A, B$  und  $C$  enthaltenden Bogen von  $J$  der Breite  $< \varepsilon_2$ ; im letzteren Falle unterscheiden wir zwei Unterfälle: 1. Es gibt einen den Punktkern  $B$  enthaltenden Bogen  $A\alpha B\beta C$  von  $J$  der Breite  $< \varepsilon_2$ , der also wiederum als  $A, B$  und  $C$  enthaltender Bogen von  $J$  der Breite  $< \varepsilon_2$  auftritt. 2. Es gibt einen Bogen  $C\gamma A$  von  $J$  der Breite  $< \varepsilon_2$ , von welchem  $B$  eine Entfernung  $> 0$  besitzt. Alsdann hat derjenige Bogen  $CB$  von  $J$ , von dem  $A$  eine Entfernung  $> 0$  besitzt, eine Breite  $> \varepsilon_2$ , so dass die Breite des Bogens  $C\gamma A\alpha B$  von  $J$  kleiner als  $\varepsilon_2$  sein muss.

<sup>1</sup>) Die Formel  $a > b$  ( $a$  grösser als  $b$ ), wo  $a$  und  $b$  reelle Grössen vorstellen, besagt in diesem Aufsätze, dass eine natürliche Zahl  $n$  angegeben werden kann, so dass  $a - b > 2^{-n}$ .

und wiederum ein  $A, B$  und  $C$  enthaltender Bogen von  $J$  der Breite  $< \varepsilon_2$  existiert. Aus der Annahme dass  $\varrho(A, C) < \frac{1}{2}\varepsilon$  und  $\varrho(C, B) < \frac{1}{2}\varepsilon$  folgt mithin für drei Punktkerne  $A, B$  und  $C$  von  $J$  immer die Existenz eines  $A, B$  und  $C$  enthaltenden Bogens von  $J$  der Breite  $< \varepsilon_2$ .

Sei nun in  $J$  eine  $\frac{1}{2}\varepsilon$ -Kette gegeben. Wenn wir je zwei aufeinanderfolgende Punkte dieser Kette durch einen Bogen von  $J$  der Breite  $< \varepsilon_2$  verbinden, erzeugen wir eine ganze (positive, negative oder verschwindende) Totalanzahl von Umläufen von  $J$ , die wir die *Ordnung* der Kette nennen. Auf Grund des Resultates des vorstehenden Absatzes wird die *Ordnung einer in  $J$  gelegenen  $\frac{1}{2}\varepsilon$ -Kette durch eine  $\frac{1}{2}\varepsilon$ -Abänderung in  $J$  nicht geändert.*

§ 2. Sei  $P$  ein von  $J$  *vollständig entfernter*, d.h. von  $J$  einen Abstand  $> 0$  besitzender Punkt. Wir wählen  $\varepsilon'' < \frac{1}{2}\varepsilon$  in solcher Weise, dass  $\varrho(P, J) > \varepsilon'' > 0$ . Sei  $\varepsilon'$  eine solche Grösse  $< \frac{1}{2}\varepsilon''$ , dass für je zwei in einer Entfernung  $< \varepsilon'$  voneinander gelegene Punktkerne  $A$  und  $B$  von  $J$  die Breite von einem der Bogen  $AB$  von  $J < \varepsilon''$  ist. Sei weiter  $\kappa^0$  eine in  $J$  gelegene *kanonische*, d.h.  $J$  genau einmal im positiven Sinne ohne Umkehrung des Richtungssinnes durchlaufende  $\varepsilon'$ -Kette und  $\kappa_2$  eine beliebige in  $J$  gelegene  $\varepsilon'$ -Kette. Alsdann kann  $\kappa_2$  in  $J$  durch eine endliche Folge von  $\varepsilon''$ -Abänderungen *in bezug auf  $\kappa^0$  kanonisiert*, d.h. in eine solche Kette  $\kappa_3$  übergeführt werden, welche aus einer ganzen (positiven, negativen oder verschwindenden), mit der Ordnung von  $\kappa_2$  identischen Anzahl von aufeinanderfolgenden mit  $\kappa^0$  zusammenfallenden Ketten besteht.

Sei  $Q$  ein Quadrat, das in seinem Inneren  $P$  und in einer Entfernung  $> \varepsilon''$  von seinem Umfang  $J$  enthält. Wir zerlegen  $Q$  in kongruente, homothetische Teilquadrate  $q$  mit einer Seitenlänge  $< \frac{1}{16}\varepsilon'$ . Unter diesen  $q$ -Quadraten wählen wir eine Teilspezies  $\tau''$  aus, welche alle in einer Entfernung  $> \frac{1}{4}\varepsilon'$  von  $J$  liegenden  $q$ -Quadrate enthält, während alle zu ihr gehörenden  $q$ -Quadrate in einer Entfernung  $> \frac{1}{8}\varepsilon'$  von  $J$  gelegen sind. Der Teilspezies  $\tau'$  fügen wir alle diejenigen  $q$ -Quadrate hinzu, welche in einem von  $\tau'$  bestimmten,  $J$  nicht enthaltenden Komplementärbereich gelegen sind, und demzufolge einen Abstand  $> \frac{1}{8}\varepsilon'$  von  $J$  besitzen. Durch diese Hinzufügung geht  $\tau'$  in eine Spezies  $\tau$  von  $q$ -Quadraten über, welche innerhalb  $Q$  nur einen einzigen Komplementärbereich bestimmt und alle in einer Entfernung  $> \frac{1}{4}\varepsilon'$  von  $J$  liegenden  $q$ -Quadrate enthält, während alle zu ihr gehörenden  $q$ -Quadrate in einer Entfernung  $> \frac{1}{8}\varepsilon'$  von  $J$  gelegen sind.

Sei  $\beta^0$  der grösste  $P$  enthaltende ganz von  $\tau$  überdeckte Bereich. Der nicht im Umfange von  $Q$  gelegene Teil der Grenze von  $\beta^0$  (ebenso wie von einem beliebigen unausdehnbaren ganz von  $\tau$  überdeckten Bereich) ist zusammenhängend und jeder seiner Punkte besitzt von  $J$  eine Entfernung  $< \frac{3}{8}\varepsilon'$  und  $> \frac{1}{8}\varepsilon'$ . Wir unterscheiden nun zwei Fälle:

1. Der Umfang von  $Q$  gehört nicht zur Grenze von  $\beta^0$ . Sei  $\kappa'$  eine aus in der Grenze  $\pi$  von  $\beta^0$  in positivem Sinne in jeweiligen

Abständen gleich  $\frac{1}{16} \varepsilon'$  aufeinanderfolgenden Eckpunkten von  $q$ -Quadraten bestehende, in  $\pi$  kanonische Kette. In bezug auf diese Kette  $\varkappa'$  (d.h. in bezug auf die aus den Verbindungsstrecken der sukzessiven Punkte von  $\varkappa'$  hervorgehende geschlossene polygonale Linie) besitzt  $P$  die Ordnung 1. Indem wir der Reihe nach jeden Punkt von  $\varkappa'$  durch einen in einer Entfernung  $< \frac{3}{8} \varepsilon'$  gelegenen Punkt von  $J$  ersetzen, erzeugen wir eine Reihe von Ketten  $\varkappa'_1, \varkappa'_2, \varkappa'_3, \dots, \varkappa'_m$ , wo  $\varkappa'_m = \varkappa''$  eine in  $J$  gelegene  $\varepsilon''$ -Kette vorstellt. Sei  $\varkappa'_p = \dots RST\dots$  und  $\varkappa'_{p+1} = \dots RS_1T\dots$ , dann kann weder das Dreieck  $RSS_1$  noch das Dreieck  $TSS_1$  den Punkt  $P$  in seinem Innern enthalten. Hieraus folgt, dass  $P$  in bezug auf  $\varkappa'_p$  und  $\varkappa'_{p+1}$  für jedes  $p$  die gleiche Ordnung, mithin auch in bezug auf  $\varkappa'$  und  $\varkappa''$  die gleiche Ordnung besitzt, so dass die Ordnung von  $P$  in bezug auf  $\varkappa''$  gleich 1 ist.

Sei  $\varkappa'_g = \dots RSU\dots$  bzw.  $\dots RU\dots$  eine in  $J$  gelegene  $\varepsilon''$ -Kette, welche durch eine  $\varepsilon''$ -Abänderung in eine in  $J$  gelegene  $\varepsilon''$ -Kette  $\varkappa'_h = \dots RTU\dots$  übergeht. Alsdann ist es ausgeschlossen, dass eines von den Dreiecken  $RST$  und  $UST$  bzw. dass das Dreieck  $RTU$  den Punkt  $P$  in seinem Innern enthält, so dass  $P$  in bezug auf  $\varkappa'_g$  und in bezug auf  $\varkappa'_h$  die gleiche Ordnung besitzt. Wenn wir also die im vorigen Absatz bestimmte Kette  $\varkappa''$  durch eine endliche Folge von  $\varepsilon''$ -Abänderungen in  $J$  in bezug auf  $\varkappa^0$  kanonisieren, erhalten wir eine in  $J$  gelegene  $\varepsilon'$ -Kette  $\varkappa$ , in bezug auf welche  $P$  noch immer die Ordnung 1 besitzt.

Wenn wir je zwei aufeinanderfolgende Punkte von  $\varkappa$  durch einen Bogen von  $J$  der Breite  $< \varepsilon''$  verbinden, erzeugen wir eine ganze Totalanzahl  $a$  von Umläufen von  $J$  darstellende geschlossene stetige Kurve  $V$ , in bezug auf welche  $P$  die Ordnung 1 besitzt, so dass  $a$  nicht verschwinden kann und die Ordnung von  $P$  in bezug auf  $J$  gleich  $\frac{1}{a}$  ist. Weil aber die letztere Ordnung eine ganze Zahl sein muss, so ist  $a$  entweder gleich  $+1$  oder gleich  $-1$ , und auch die Ordnung von  $P$  in bezug auf  $J$  entweder gleich  $+1$  oder gleich  $-1$ .

2. Der Umfang von  $Q$  gehört zur Grenze von  $\beta^0$ . Alsdann kann  $P$  durch eine in einer Entfernung  $> 0$  von  $J$  gelegene unendliche polygonale Linie mit dem Unendlichen verbunden werden, so dass die Ordnung von  $P$  in bezug auf  $J$  gleich 0 ist.

Aus den für die obigen Fälle 1. und 2. hergeleiteten Ordnungseigenschaften folgt, dass für einen beliebigen von  $J$  vollständig entfernten Punkt  $P$  die Entscheidung zwischen den Fällen 1. und 2. unabhängig von der Wahl der (den Bedingungen  $\varepsilon'' > 0$ ,  $\varepsilon'' < \frac{1}{2} \varepsilon$  und  $\varepsilon'' < \varrho(P, J)$  genügenden) Grösse  $\varepsilon''$  ausfällt.

§ 3. Seien  $P_1$  und  $P_2$  zwei von  $J$  vollständig entfernte Punkte. Wir unterscheiden drei Fälle:

1.  $P_1$  und  $P_2$  befinden sich beide im ersten Falle von § 2. Alsdann wählen wir  $\varepsilon''$  in sowohl für  $P_1$  wie für  $P_2$  passender Weise,

d.h. so dass sowohl  $P_1$  wie  $P_2$  eine Entfernung  $> \varepsilon''$  von  $J$  besitzt, und bestimmen nach § 2 ein entsprechendes Quadrat  $Q$ , eine entsprechende Spezies  $\tau$  von  $q$ -Quadraten, und in  $\tau$  die zu  $P_1$  bzw.  $P_2$  gehörigen Bereiche  $\beta_1^0$  und  $\beta_2^0$ . Wären nun  $\beta_1^0$  und  $\beta_2^0$  verschieden, dann besässe  $P_2$  in bezug auf  $\varkappa'_1$  die Ordnung 0, mithin der Reihe nach auch in bezug auf  $\varkappa_1''$ ,  $\varkappa_1$ ,  $V_1$  und  $J$  die Ordnung 0. Aus diesem Widerspruche folgern wir, dass  $\beta_1^0$  und  $\beta_2^0$  identisch sind, dass also  $P_1$  und  $P_2$  durch einen von  $J$  vollständig entfernten endlichen Streckenzug verbunden werden können.

2.  $P_1$  und  $P_2$  befinden sich beide im zweiten Falle von § 2. Alsdann wählen wir wiederum  $\varepsilon''$  in sowohl für  $P_1$  wie für  $P_2$  passender Weise, und bestimmen nach § 2 ein entsprechendes Quadrat  $Q$  und eine entsprechende Spezies  $\tau$  von  $q$ -Quadraten. Hierauf kann sowohl  $P_1$  wie  $P_2$  durch einen von  $J$  vollständig entfernten endlichen Streckenzug mit dem Umfang von  $Q$  verbunden werden, so dass  $P_1$  und  $P_2$  auch untereinander durch einen von  $J$  vollständig entfernten endlichen Streckenzug verbunden werden können.

3. Von den Punkten  $P_1$  und  $P_2$  befindet sich der eine im ersten, der andere in zweiten Falle von § 2. Alsdann ist die Existenz eines von  $J$  vollständig entfernten,  $P_1$  und  $P_2$  verbindenden Streckenzugs ungereimt, weil auf einem derartigen Streckenzuge einerseits alle Punkte gleiche, andererseits die Punkte  $P_1$  und  $P_2$  verschiedene Ordnungen in bezug auf  $J$  haben müssten.

Diejenigen von  $J$  vollständig entfernten Punkte, die sich im ersten bzw. im zweiten Falle von § 2 befinden, nennen wir *positiv-innere* bzw. *positiv-äussere* Punkte von  $J$ .

§ 4. Positiv-äussere Punkte von  $J$  lassen sich in mannigfacher Weise unmittelbar angeben. Einen positiv-inneren Punkt von  $J$  bestimmen wir wie folgt:

Sei  $\varepsilon$  der in § 1 formulierten Forderung entsprechend gewählt, und  $\varepsilon''$  eine der Beziehung  $\frac{1}{3}\varepsilon > \varepsilon'' > 0$  genügende Grösse. Sei  $\varepsilon'$  im Anschluss an  $\varepsilon''$  so gewählt, dass der im ersten Absatz von § 2 angegebenen Beziehung zwischen  $\varepsilon'$  und  $\varepsilon''$  genügt wird. Sei  $Q$  ein Quadrat, das in einer Entfernung  $> \varepsilon''$  von seinem Umfang  $J$  in seinem Inneren enthält. Zu  $Q$  und  $\varepsilon'$  konstruieren wir nach der im zweiten Absatz von § 2 angegebenen Methode eine entsprechende Spezies von  $q$ -Quadraten  $\tau$ . Sei  $\beta_1$  der grösste an den Umfang von  $Q$  grenzende, ganz von  $\tau$  überdeckte Bereich. Dieser Bereich  $\beta_1$  bestimmt innerhalb  $Q$  einen einzigen Komplementärbereich  $K$ , der  $J$  enthält und dessen Grenze zusammenhängend ist. Wir wollen einen Augenblick annehmen, dass jedes in einem sowohl zu  $K$  wie zu  $\tau$  gehörigen Bereich enthaltene, aus  $q$ -Quadraten bestehende Quadrat eine Seitenlänge  $< \frac{1}{11}\varepsilon$  besitzt.

Alsdann hat jeder Punkt von  $K$  eine Entfernung  $< \frac{3}{8}\varepsilon' + \frac{1}{8}\varepsilon$  von  $J$ . Hieraus folgern wir, dass die im ersten Absatz von § 2 definierte kano-

nische  $\varepsilon'$ -Kette  $\varkappa^0$  sich mittels einer endlichen Folge von zunächst  $\varepsilon''$ -Abänderungen und sodann  $(\frac{3}{4}\varepsilon' + \frac{1}{4}\varepsilon)$ -Abänderungen in  $J$ , mithin mittels einer endlichen Folge von  $\frac{1}{2}\varepsilon$ -Abänderungen in  $J$ , in eine aus einem einzigen Punkt von  $J$  bestehende singuläre Kette überführen lässt. Dies aber widerspricht der am Schluss von § 1 formulierten Eigenschaft. *Es gibt also einen solchen unausdehnbaren, ganz von  $\tau$  überdeckten, nicht an den Umfang von  $Q$  grenzenden Bereich  $\beta$ , in welchem ein aus  $q$ -Quadraten bestehendes Quadrat  $g$  der Seitenlänge  $> \frac{1}{16}\varepsilon - \frac{1}{4}\varepsilon'$  enthalten ist.*

Ein zum Mittelpunktkerne von  $g$  gehöriger Punkt  $P$  genügt der Beziehung  $\varrho(P, J) > \frac{1}{8}\varepsilon$ , so dass für die Entitäten  $P$ ,  $\varepsilon''$  und  $\varepsilon'$  dieses § alle für die im § 2 eingeführten Entitäten  $P$ ,  $\varepsilon''$  und  $\varepsilon'$  daselbst geforderten Beziehungen bestehen. Auf Grund der ersten drei Absätze des § 2 *erscheint mithin der Bereich  $\beta$  als grösster  $P$  enthaltender, ganz von  $\tau$  überdeckter Bereich  $\beta^0$ , und befindet sich als solcher im ersten der beiden dortigen Fälle, d. h. wir erkennen in  $P$  einen positiv-inneren Punkt von  $J$ .*

§ 5. Unter einem *stetigen Kurvenbogen* verstehen wir eine ebene Kernspezies, welche eindeutiges, mithin gleichmässig stetiges Bild des (als Kernspezies zu betrachtenden) Einheitsintervalles der  $X$ -Achse ist.

Unter einem *Jordanschen Kurvenbogen*  $F$  verstehen wir einen stetigen Kurvenbogen, der als Abbildung des Einheitsintervalles der  $X$ -Achse eine stetige (mithin eindeutige und gleichmässig stetige) Umkehrung besitzt.

Sei  $P$  ein von  $F$  vollständig entfernter Punkt. Wir wählen  $\varepsilon''$  in solcher Weise, dass  $\varrho(P, F) > \varepsilon'' > 0$ . Sei  $\varepsilon'$  eine solche Grösse  $< \frac{1}{2}\varepsilon''$ , dass für je zwei in einer Entfernung  $< \varepsilon'$  voneinander gelegene Punktkerne  $A$  und  $B$  von  $F$  die Breite des Bogens  $AB$  von  $F$   $< \varepsilon''$  ist. Alsdann kann eine beliebige in  $F$  gelegene  $\varepsilon'$ -Kette in  $F$  durch eine endliche Folge von  $\varepsilon''$ -Abänderungen *zusammengezogen*, d. h. in eine aus einem einzigen Punkte bestehende "singuläre Kette" übergeführt werden.

Sei  $Q$  ein Quadrat, das in einer Entfernung  $> \varepsilon''$  von seinem Umfang  $F$  in seinem Innern enthält. In analoger Weise wie im § 2 konstruieren wir in  $Q$  die  $q$ -Quadrate, und bilden eine Spezies  $\tau$  von  $q$ -Quadraten, welche innerhalb  $Q$  nur einen einzigen Komplementärbereich bestimmt und alle in einer Entfernung  $> \frac{1}{4}\varepsilon'$  von  $F$  liegenden  $q$ -Quadrate enthält, während alle zu ihr gehörenden  $q$ -Quadrate in einer Entfernung  $> \frac{1}{8}\varepsilon'$  von  $F$  gelegen sind. Sei  $\beta^0$  der grösste  $P$  enthaltende ganz von  $\tau$  überdeckte Bereich. Nehmen wir an, dass der Umfang von  $Q$  nicht zur Grenze von  $\beta^0$  gehört, und erörtern wir diese Voraussetzung analog wie im § 2. Alsdann gelangen wir zu einer in  $F$  gelegenen  $\varepsilon'$ -Kette  $\varkappa''$ , in bezug auf welche  $P$  die Ordnung 1 besitzt. Wenn wir aber durch eine endliche Folge von  $\varepsilon''$ -Abänderungen diese Kette  $\varkappa''$  in eine aus einem einzigen Punkte bestehende singuläre Kette  $\varkappa$  überführen, dann muss die Ordnung von  $P$  in bezug auf  $\varkappa$  einerseits gleich 1, andererseits gleich 0 sein. Aus diesem Widerspruche ergibt sich, dass *der Umfang*

von  $Q$  notwendig zur Grenze von  $\beta^0$  gehören muss, und hieraus nach der Methode des § 3 weiter, dass je zwei von  $F$  vollständig entfernte Punkte durch einen von  $F$  vollständig entfernten Streckenzug verbunden werden können.

Wenn wir jetzt zur Jordanschen Kurve  $J$  zurückkehren, so folgt aus dem vorstehenden Absatze, dass für einen beliebig kleinen Teilbogen  $\beta$  von  $J$  ein beliebiger positiv-innerer und ein beliebiger positiv-äusserer Punkt von  $J$  durch einen vom Komplementärbogen von  $\beta$  in  $J$  vollständig entfernten endlichen Streckenzug verbunden werden können. Mittels einer kurzen Ueberlegung folgt hieraus weiter, dass zu einem beliebigen Punktkern  $A$  von  $J$  sowohl eine gegen  $A$  positiv konvergierende Folge von positiv-inneren Punkten von  $J$  wie eine gegen  $A$  positiv konvergierende Folge von positiv-äusseren Punkten von  $J$  konstruiert werden kann, m. a. W. dass jeder beliebige zu  $J$  gehörige Punkt sowohl Grenzpunkt von positiv-inneren wie Grenzpunkt von positiv-äusseren Punkten von  $J$  ist.

Sei  $G_1$  die Spezies der positiv-inneren,  $G_2$  die Spezies der positiv-äusseren Punkte von  $J$ . Alsdann muss jeder Grenzpunkt von  $G_1$  abweichen von  $G_2$  und jeder Grenzpunkt von  $G_2$  abweichen von  $G_1$ . Sei  $\gamma_1$  die Grenze von  $G_1$ , d.h. die Spezies der von  $G_1$  abweichenden Grenzpunktkerne von  $G_1$  und  $\gamma_2$  die Grenze von  $G_2$ , d.h. die Spezies der von  $G_2$  abweichenden Grenzpunktkerne von  $G_2$ . Auf Grund des Resultates des vorigen Absatzes gehört dann jeder Punktkern von  $J$  sowohl zu  $\gamma_1$  wie zu  $\gamma_2$ . Andererseits folgt aus der am Anfang des laufenden Absatzes befindlichen Aussage, dass jeder Punktkern von  $\gamma_1$  sowie jeder Punktkern von  $\gamma_2$  einen Abstand Null von  $J$  besitzen, mithin zu  $J$  gehören muss.

Somit ist sowohl von der Spezies der positiv-inneren wie von der Spezies der positiv-äusseren Punkte von  $J$  die Grenze mit  $J$  identisch.

**Hystology.** — "*On collagenous fibrils: their origin, structure and arrangement.*" By G. C. HERINGA and H. A. LOHR. (Communicated by Prof. J. BOEKE.)

(Communicated at the meeting of Oct. 25. 1924).

The paraffin-, and celloidin-technique has in course of time come to be looked upon as an infallible method, so that implicit confidence is placed in the histological images thereby obtained. Sometimes, however, their reliability must be called in question, when we see that the various current hypotheses concerning the structure of connective tissue have been based on observations of material that suffered considerably from the deleterious influence of the embedding method. Two factors, viz dehydration and heating are answerable for this injury. Their intense influence may be readily conceived when comparing a carefully made paraffin-preparation with one that has been embedded in gelatin and cut on the freezing-microtome. Then it will appear that the injury done to the structure of the connective tissue by the said influences, is greater than in other more cellulous tissues. This injury increases with the augmentation of collagenous fibrils in the tissue. With justice we may here denounce the incriminated methods on account of the difficulty to obtain with them good preparations of organs such as tendon and skin, which have almost entirely been made up of highly fibrillous connective tissue. In the paraffin-sections of the skin the fibrilbundles are shrivelled up into shapeless lumps leaving wide interstices. In consequence of the shrinking a tendon of some thickness is apt to grow so hard, that cutting it is altogether out of the question. The cells of the connective tissue are also involved in the general ruin. During the shrinking of the fibrils, surrounding them, they are torn asunder to all sides. What remains of them is only a number of scattered pieces and fragments, only the nuclei can be discerned in a hematoxylin-eosin preparation amidst the red-stained chaos. This aspect has become so familiar to authors that they have gradually forgotten, that the technique adopted destroyed the tissue and they have based on their observations of mutilated cell-rests the conclusion that fibroblasts, after accomplishing their task of producing fibrils, are "physiologically degenerated". This conclusion is absolutely wrong! True, unlike the fibrillar connective tissue, the young wide-meshed connective tissue presents with the same paraffin-technique beautiful branched cells, and these cells screen themselves from observation according as the fibrils accumulate around them. (FLEMMING's images). For this fact, however, an equally plausible explanation may be found, when con-

sidering that the fibril-poor tissue is far less sensitive to the hurtful influence of the method than the collagenous fibrils. This is the only possible conclusion when we consider that in gelatin-sections, where shrinking from dehydration does not take place, in the collagenous fibres, no "degenerative" modifications of the connective tissue-cells are at all noticeable, and that, on the other hand, also in "adult" connective tissue the cells appear as perfectly vital protoplasm-rich elements, which are just as much as their mesenchymal progenitors interconnected on all sides by their branches. In previous publications <sup>1)</sup> one of us has discussed the cells of connective tissue in extenso. We should not have mentioned it here, if not, as stated just now, some authors are inclined to associate that presumed cell-evolution with a "fibroblastic" function of the cell.

In the gelatin-freezing-sections of the skin the interspaces between the cells are so of collagenous fibres, that at best only inappreciably small capillary interstices are available for tissue-lymph. Instead of the chaos of the paraffin-sections we find here well-defined bundles of fibres, known also from the "artificial oedema preparations", which form as yet an inextricable closely packed network. The spatial orientation of the cells inter se and their branches on the one side, and on the other that of the intertwining collagenous bundles between the cells, is so complicate that it is simply impossible to establish a directly genetical connection between cells and fibres. This conviction, which urged itself upon us the moment we took cognizance of gelatin-sections of connective tissue, induced us to try to prove, with our technique, the old hypothesis of NÄGELI, who maintained that the fibres appear spontaneously in the interstitial substance. Our gelatin technique gave us an advantage over the authors who also tried before us to abandon the "fibroblastic" theory (v. EBNER, MERKEL and others) while, moreover, we found a powerful aid in the application of dark-ground microscopy. While our embedding method guarded the fibres from shrivelling and clotting, dark-ground microscopy enabled us to demonstrate the formation of extremely fine (ultramicroscopic) collagenous elements in regions where not a trace of them could be recognized with the ordinary illumination; SIEDENTOPF's "Wechsel-condensor" did inestimable service. Until some weeks ago we were ignorant of the existence of SZEGVARI's "Azimuthblende". Therefore, when trying to recognize the fibrils on the basis of SIEDENTOPF's <sup>2)</sup> and KRUYT's <sup>3)</sup> researches, we made use of a unilateral illumination by inserting a slit-screen. Especially when, moreover, the peripheral rays are intercepted with the iris, the results are usable, though we must admit that the adjustable "Azimuthblende" of SZEGVARI is far preferable. Be this as it may, we have attained also with our somewhat primitive instruments a few results that will be reported below. Our material

1) HERINGA, Ned. Tijdschr. v. Geneesk. 1922, '23 and '24.

2) SIEDENTOPF, Z. W. Mikrosk. Bd. 29, 1912.

3) KRUYT, These Proceedings 24, 1664, 1916.

consisted in umbilical cords and skin of sheep and man of various life-periods.

1. (umbilical cord sheep's embryo 2.3 cm). When collagenous fibrils appeared, we signalled in an initial stage the appearance of diffuse Tyndal-light in the interstitial substance, in places where neither with common illumination, nor with dark-ground illumination fibrils could be distinguished. They were visible, however, in the neighbourhood of fibrillar formations. Rotation of the slit screen revealed the presence of needle-shaped ultramicrosomes.

2. Already in the youngest of the available umbilical cords, the same we referred to above, we found fibrils anywhere in the interstitial substance.

Large masses of fibrils, coming directly into view with light-ground, are disposed round the cells and their prolongations like inextricable clews, leaving the cells in their midst intact. Fine-spun fibrils, only visible in dark-ground are everywhere seen isolated or in groups, also at a large distance from the cells. Individually they proceed in a strongly curving line, so that, when they are proceeding in groups, they are intertwined in a very complicated way.

3. In many places in the youngest umbilical cord, and everywhere in the older ones a tendency to orderly arrangement in the fibril-complexes may be noted resulting in the formation of bundles of fibrils running in the same direction. These bundles are never cylindrical. From their very origin to the stage of the fully developed connective tissue they are tape-shaped, i.e. the fibrils do not range themselves evenly on all sides, not cylindrically, but exclusively or at any rate by preference, in a plane, the one beside the other. Just like the individual fibrils above-discussed, the course of the tapes is complicate and twisted. This is very likely due to the ultrastructure of the fibrils themselves, because, as has been stated before, the morphological character of the bundles is so irregular as to preclude any responsibility of the individual cells in this respect, even though the most strongly developed fibrillar formations are always found in the neighbourhood of the cells. We detected in our preparations MERKEL'S images of fibril-masses in the environment of the cells. On closer inspection these fibrilmasses always appeared to consist of intertwined and anastomotic fibril-tapes, mostly gathered into films.

4. In contradistinction to the irregularity in the course of the individual collagenous fibrils and their tapes (in umbilical cord and skin), the regularity with which the tapes are united into one whole of three dimensions implies a compliance with certain laws, which we have not yet been able to analyse, but which undoubtedly points to a three-dimensional architecture in the differentiation of the interstitial substance as well as in the disposition of the cells<sup>1)</sup>.

5. To sum up we arrive at the provisional conclusion that the collage-

<sup>1)</sup> HERINGA, l. c.

nous fibrils in the interstitial substance originate from needle-shaped ultramicrones ranging themselves in area extent; secondly that the interstitial substance does not induce the formation of fibrils everywhere in an equal degree; further that *ceteris paribus* the environment of the cells are selected by preference for the distribution of the fibril-masses; also that cells exert no influence upon the course of the fibrils; and finally that the tendency of fibrils to a peculiarly sinuous course, as well as their habit to form close tapelike complexes must arise from physical properties of the fibrils themselves.

We do not disguise from ourselves, though, that the above conclusions are extremely fragmentary, and that our present achievement is but the first step on an endless field of research. Meanwhile taking into consideration that the results of our work of nearly two years, inadequate though they may be, seem to be fairly complementary to the researches made by others in a similar domain, we feel justified in publishing our view as a basis for subsequent investigation.

As stated before, our working hypothesis was the well-known hypothesis of NÄGELI who imagined the collagenous fibrils to be rows of micellae.

Already many years ago this ingenious hypothesis was substantiated by the inquiries of AMBROSE and his pupils. It was, moreover, corroborated pre-eminently in the röntgenographic researches of HERZOG, JANCKE and others, who on the principle suggested by LAUE, established for good and all the micellar formation of a number of organic fibrillar structures and also of the collagenous fibrils. Some months ago we also started, apart from HERZOG, a röntgenological investigation of the tendon; we were benefited in our endeavours by Dr. KOLKMEIJER's knowledge and his instrument which he kindly placed at our disposal. For the present this investigation seems to confirm HERZOG's results, so that we are encouraged to pursue it.

If we consider how, when seen in the light thrown upon them by the röntgenological investigations alluded to, the fibril assumes completely the character of a crystalline formation, we cannot be surprised that this induced several authors to call the origin of fibrils a crystallization-process, their main point of consideration then being that it must be in virtue of intermicellar forces that the ultramicrones "eine gesetzmäßige Anordnung einnehmen" <sup>1)</sup>). The more we look about us in living nature, the more we are impressed with the idea that the orderly arrangement of the micellae is one of the chief resources of nature to attain the formation of sharply differentiated structural elements. It is especially the fibrils with their row of micellae that come into play in a great number of modifications in living nature.

So while of late years the hypothesis that collagenous fibrils consist of ultramicrones arranged in a row, has gained ground more and more, in histology the conception of the origin of connective-tissue fibres remains

<sup>1)</sup> SCHMIDT. „Die Bausteine des Tierkörpers im polarisierten Lichte". 1924.

circumscribed within the field of old speculations. Our inquiry of which the results have been recorded above, is intended for an effort to assign to physical data the influence on histology that is properly due to them.

While on the one hand we succeeded in identifying the origin of the collagenous fibrils as a "crystallization" process that progresses spontaneously in a given environment, on the other hand their arrangement in the interstitial substance remains a puzzle. We know, indeed, for certain from the analytical work of ROUX *c.s.*, and from the experimental work of LERICHE, that external mechanical factors exert a great influence upon the disposition of fibrils; however, when examining the complex fibril-texture of, say, the skin, we see at a glance that, besides external factors also intrinsic forces come into play. We here wish to emphasize one of the peculiar behaviours of collagenous fibrils, *viz.* the formation of bundles. It has been known long since that collagenous fibrils display a tendency in their joint-course to combine into bundles. This has also raised the supposition of splitting of fibrils. It seems strange, however, that, so far as I know, workers have never thoroughly considered the fact that the bundles are not round but always flat like a tape. Still, these details have often been distinctly represented in many pictures, e.g. in V. EENER's and LAGUESSE's publications. As regards the forces that keep these fibrilbundles together, histologists speak of a sticky substance encasing the fibrils. In the recently published work by SCHMIDT (*l. c.*), which for the rest is so much up-to-date, this term is met with again and again.

We have suspected that the peculiar junction of the fibrils, just as well as that of the micellae, may take origin in the specific properties of the fibrils themselves. We are the more disposed to think so since SZEGVARI<sup>1)</sup> found in various threadforming colloids a number of unidirectional bundles of filiform elements. In our endeavour to find an analogy between the observations of SZEGVARI and ours we are prompted to consider more narrowly the collagenous fibrils and their origin, from a collochemical point of view.

It need not be argued that gelatinous fibril-poor interstitial substance, such as is typical of embryonic connective tissue, is of a colloidal nature. It is also a fact, however, that the collagenous fibres, which we see appear increasingly in this interstitial substance, also reveal the typical properties of colloids. The sensitivity to dehydrating means, referred to at the outset, has justly convinced NÄGELI that the micellae, which as stated above, make up the fibrils, must be enclosed in water. The current opinion now is, that a water-envelop belongs to all protein bodies in colloidal solution, (emulsoids).

Now, when concluding on the basis of the arguments enumerated above, that these fibrils have not been introduced into the intercellular substance

<sup>1)</sup> SZEGVARI. Ueber die ultra mikroskopische Untersuchung linearer Elemente. I u. II *Zeitschr. f. phys. Chemie*, 112. (1924).

from the outside (i.e. from the cells) but have originated there spontaneously through methodical conjunction of isolated particles; moreover, when reflecting that, as fibrillation progresses, the consistency of the connective tissue increases and its water-content decreases in the course of the histogenesis; when all these facts are considered collectively, then it is conceivable that we should designate the change, accomplished in the interstitial substance as a gelification. We are the more entitled to do so as in collochemistry gel is defined as a precipitation of hydrated particles, which definition is quite applicable to the process under consideration. A peculiar feature of this case, however, is that the particles close up more firmly in one spatial direction than in the other two. From the above observations regarding a systematic grouping of the fibrils, it may be inferred that also in the other two directions there is decidedly a system in the orientation of the particles. This, in our opinion, is an additional argument for defining connective-tissue as a thread-forming gel.

In colloid chemistry we know a number of substances in which the precipitation of particles also gives rise to filiform fibrillation (soap, vanadium pentoxid). We do not quite see why SZEGVARI, contrary to the current opinion, speaks of threadforming sols, and not of threadforming gels. SZEGVARI himself detected, as we observed just now, in these "sols" a constancy of every individual group in the orientation of the threads *inter se*. If this formation of bundles is of more frequent occurrence in our preparations than in those of SZEGVARI, which has convinced us of the existence of a systematic three-dimensional structure, we cannot help observing at the same time, that the histological technique, which has been so much disputed, offers the advantage of affording some insight into spatial structures, which are of necessity lost in the preparations of the colloid-chemists. This very consideration prompted us to publish our views after reading SZEGVARI's publications. In view of the grounds for considering connective tissue as a thread-forming colloid, it would seem to us that our preparations are apt to render SZEGVARI's observations more conspicuous.

Finally we intend to set forth hypothetically how we would imagine the structure of collagenous fibrils from a colloidchemical point of view. It would appear to us, as we shall endeavour to prove, that this speculation affords a satisfactory explanation of a number of well-known physical properties of collagenous substance.

Of course we started again from NÄGELI's hypothesis concerning the formation of fibrils from a linear succession of particles. The result obtained with polarized light (AMBRONN, SCHMIDT and others) together with our observations with dark-ground illumination (*vide supra*) warrant the assumption, that just as in the case of threadgels (SZEGVARI) and fibrin (HEKMA), also in the case of collagenous fibres the micellae are rod-shaped and ellipsoidal. The micellae, being emulsoids, are further possessed of two stabilityfactors, viz. 1<sup>o</sup> a micellar electrical charge and 2<sup>o</sup> a water-envelop.

Finally we also feel inclined to assume that the elongated micellae have beyond their micellar charge also a polar charge of opposite sign at their extremities, which charge we hold to be answerable for the arrangement of particles in rows. The size of the particles, the distance of which will, as we hope, be elucidated by our röntgenphoto's, we suppose to be amicronic. Supposing the water-envelop to be an unimolecular layer we might illustrate the micellae with their water-layer by the following diagram. (Fig. 1. to the left of the bracket).

It goes without saying that such micellae will attract each other with their unlike poles. But more is to happen. The micellae impart to their water-layer a charge that must induce adsorption of ions from the enviring fluid and the occurrence of an electric double-charge along the water-surface. The presence of the polar charges will be the cause that this electric double-layer is not of the same compactness all along the water-surface, but that a larger number of ions will accumulate at the poles than along the side-walls. This larger accumulation of ions at the poles will lower the surface tension there.

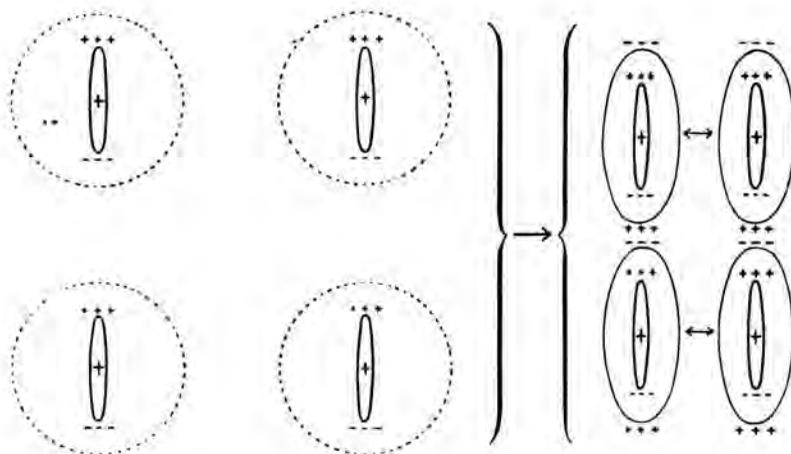


Figure 1.

The consequence is that opposite the poles the curvature of the water-envelop is more pronounced and consequently is getting ellipsoidal also round the micella.

This alters at the same time the influence which the ions exert upon each other in space. If this influence were restricted to the expelling (stabilizing) action of the like charges of ions, the micellae would in virtue of their polar charges (in case they extend in the same direction, like a tendon) dispose themselves in all directions at the same distance from each other. But there is another complicating influence at work, viz. the mutual attraction of the highly distended sidewalls of the water-envelops. Repulsion by micellar charge, attraction by the water-envelops, these two

counteracting forces bring about the actual distribution of the fibrils in space. The relation between these forces is to account for the tendency of the

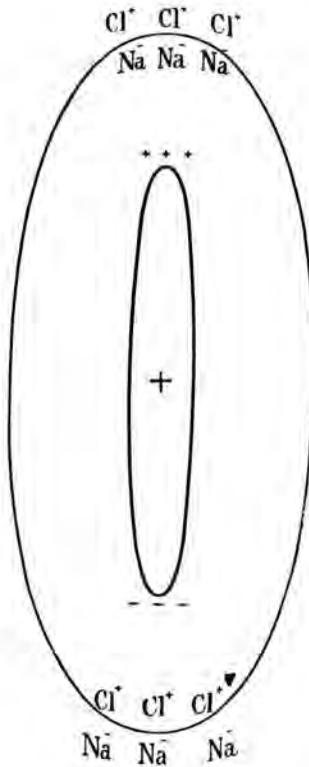


Figure 2.

fibrils to form bundles. That the fibril-bundles are not cylindrical but tape-like, implies that the attraction of the fibrils is more intense in the one spatial direction than in the other. This again involves that also the transverse section of the water-envelop (vertical to the long axis of the micella) has the form of an ellipse. In harmony with this the fibrils are not, as has often been represented, uniaxial, but according to SCHMIDT biaxial birefringent. If this reasoning is correct, the mutual influence of the ions in space might be figured as shown to the right of the brackets in fig 1. It appears to us that our exposition of the structure of the collagenous fibrils offers a plausible explanation of a number of physical properties they possess.

1<sup>o</sup> Their faculty of swelling in a faintly acid and in a faintly alkaline environment.

Given the tension elicited by the polar charges in the ellipsoidal water-envelop, that envelop will display a tendency to become spherical. This can be only when the surface tension of the sidewalls may diminish relative

to the polar curvatures. Given also the fact that, as we suppose, the polar charges of the envelop are stabilized by those of the micella, an increase of the curvature of the sidewalls is possible only if from the outside ions can be transmitted to the surface, i.e. by supplying free + ly or - ly charged ions. If, however, under these circumstances the sidewalls are to be globed, this will be possible only with increase of the volume of the whole enveloping ellipsoid, i.e. with an adsorption of water (acid-, and alkali-swelling). A shortening of the long axis is hardly required here, and will take place only when at length the side charges approach those of the poles, and thereby the whole tends to be globular. Indeed, with acid-swelling a slight but distinct shortening manifests itself.

Two factors will co-operate to bring about a thickening of the tendon with acid-hydration: 1<sup>o</sup> the lengthening of the short axis of the ellipsoidal water-envelops themselves; 2<sup>o</sup> the increasing expulsion of the fibrils by their like micellar charges, in proportion to the decrease of attraction of the curving water-surfaces. In agreement with this is the fact that with increasing hydration of the connective tissue (edema) the fibril-bundles are

gradually discomposed. The fibril-isolating action of line and baryt-water, hitherto ascribed to "sticky matter being dissolved", might also be plausibly interpreted in an analogous way by the accumulation of ions of the water-envelops.

2<sup>o</sup> The shortening of the long axis will, however, be more pronounced, if *without wateradsorption* the particles can contract into a sphere. According to the conception put forward this would be possible only with abolishment of the polar charge, that is to say, since the polar charge of the water-envelop is secondary to that of the micellae, with abolishment of the latter. Well then, whereas the reversible hydration-swelling, as stated before, involves only a relatively insignificant shortening, we see a tendon contrast suddenly in warm *neutral* water at 60° (the temperature for denaturation of protein!). Does not this phenomenon point to a discontinuance of a tension, which may the more readily be attributed to molecular changes of the micella, if we add to what has been said, that the changes appearing in the birefringence are in this case not reversible, and that, through distention, only a part of the original "Stäbchen Doppelbrechung" can be recovered?

3<sup>o</sup> That reversible to less than 60° shortening of a tendon caused by heat is to be explained by rounding of the ellipsoidal micellae, is a conclusion based long since on the changes occurring in the double refraction. This rounding which in the first instance we think fit to localize in the water-envelops, we might ascribe to decrease of the surface-tension of the water-envelops, which thereby are forced to intenser curving.

In the foregoing we have set forth that with our hypothesis an explanation may be given of a number of properties of collagenous fibrils. It occurs to us that by the same reasoning, when applied to other fibrils, e.g. muscle-, and nerve-fibres, whose analogous structural development from a row of micellae has been established by röntgenologic investigation, several physiological facts may be elucidated. It would be premature, however, to go into that problem now. We know quite well that our reasoning is purely hypothetical. It may be that principles of colloid-chemistry have not been stabilized enough to apply its definitions and speculations at this moment to the immensely complicated systems in living nature. It may also be that we, being laymen, have with our lack of experience misused principles, of themselves unexceptionable. We trust that, even if the theoretical speculation, to which the second half of our paper has been devoted, should be invalidated by the critique of more competent observers than ourselves, the observations of the facts recorded in the first half will at any rate be admitted to be unexceptionable. Our endeavour to refer connective tissue to the domain of colloid-chemistry will not be made in vain if it would help to convince biologists, that also outside of protoplasm there can be question of life, in which genesis, existence and dissolution succeed each other according to fixed laws.

**Mathematics.** — "On a Group of Representations of the Linear Complex of Rays". By M. N. VAN DER BIJL. (Communicated by Prof. JAN DE VRIES).

(Communicated at the meeting of April 25, 1925).

§ 1. We have in view all the representations of a linear complex  $L$  on the points of space for which each ray contains its own image. These have a number of properties in common of which the most important follow here. In the first place these two:

a. A plane pencil out of  $L$  is represented on a conic  $k^2$  through the null point of the plane of the pencil which is touched at this point by the ray that has its image in the point.

b. The image of a net of rays out of  $L$  is a cubic surface  $O^3$  through the directrices of the net ( $u$  and  $v$ ).  $O^3$  has the image of  $u$  as double point if  $u$  belongs to  $L$ .

Proof of a: the image curve is plane, has a single point in the null-point, and cuts any ray of the pencil, besides, in the image point of this ray.

Proof of b: A plane  $v$  through  $u$  contains of the image surface the conic  $k^2$  that corresponds to the pencil in  $v$ , and  $u$  itself (each point of  $u$  corresponds as image to one ray of the net). The same holds good for  $v$ , the polar line of  $u$ . If  $u \equiv v$  is a complex ray, the other part of the intersection,  $k^2$ , continues to pass through the image point of  $u$  if  $v$  turns round  $u$ . This point is, therefore, a node of  $O^3$ .

## § 2. The singular figures.

If  $v$  turns in the indicated way,  $k^2$  degenerates 5 times into a pair of lines, according to a well known property of the cubic surfaces. The vertices of complex-plane pencils with degenerate image curves form, therefore, a surface of the fifth order; for the arbitrary line  $v$  contains 5 of these vertices. As the degeneration occurs only when the corresponding plane pencil contains a singular ray,  $v$  is cut by 5 such rays; in other words: there exists a scroll of the fifth order  $R^5$ , of singular rays (*singular scroll*). It coincides with the surface of the fifth order mentioned above.

The nodal curve  $\delta$  of this surface is the locus of the singular points (*singular curve*), for a point on  $\delta$  is among others the image of 2 singular rays and, inversely, through any singular point there must pass 2 singular rays, to wit the pair into which  $k^2$  degenerates for this point.

Let  $S$  be a point of  $\delta$ ,  $s_1$  and  $s_2$  the 2 singular rays through  $S$ . A

plane  $\nu$  through  $s_1$  cuts  $R_s^5$  along a figure of the fifth order consisting of  $s_1$  and a curve of the fourth order which cuts  $s_1$  in the point of contact of  $\nu$  and in 3 more points, including  $S$ , which belong to  $\delta$ . Applying the same to  $s_2$  we find in all 5 points  $(\delta, \nu)$ . A point  $P$  of  $\nu$  outside  $s_1$  and  $s_2$  cannot belong to  $\delta$ , for then the complex ray  $SP$  would be singular so that the image of the plane pencil  $S$  would become a figure of the third order. In this way we have found:

*There exists a singular scroll of the fifth order with a nodal quintic as singular curve ( $\delta^5$ ).*

Considering these figures we may add to property  $I_a$  that  $k^2$  is wholly defined by the 5 points of intersection of  $\delta_s^5$  and the plane of the pencil; and to  $I_b$  that  $O^3$  contains 5 singular rays, to wit the images of the points  $(u, R_s^5)$ , and further the whole curve  $\delta_s^5$ , because each of its points corresponds as image to the ray of the net passing through it.

§ 3. *a. Image of a point-range  $u$ .* Let  $\nu$  be again the associated polar line. A plane  $\nu$  through  $u$  contains 2 generatrices of the image: the 2 rays that join the nullpoint  $(\nu, \nu)$  to the points of intersection  $(k^2, u)$ . Through any point of  $u$  there passes one generatrix: the image ray of that point. Accordingly we find a cubic scroll  $R_u^3$ , that has  $u$  as single,  $\nu$  as double directrix. To the points  $(R_s^5, u)$  there correspond 5 image rays, which are common generatrices of  $R_s^5$  and  $R_u^3$ . If  $u$  is a complex ray,  $R_u^3$  becomes a surface of CAYLEY, for in this case  $u$  is a directrix and at the same time a generatrix.

*b. Image of a field of points  $V$ .* The conic which represents the plane pencil through an arbitrary point or in an arbitrary plane, cuts  $V$  in 2 points. Hence the locus of the image rays is a congruence [2,2]. 16 plane pencils belong to this. In the first place the pencil in  $V$ ; further 5 plane pencils with vertices in  $(V, \delta_s^5)$ ; the remaining 10 lie in the planes in which  $k^2$  has one of the 10 joins of these vertices as a non-singular component. Non-singular component of a degenerate  $k^2$  can be all the chords  $k$  of  $\delta_s^5$  in the plane through  $k$  and the singular ray through the point  $(k, R_s^5)$  outside  $\delta_s^5$ . The congruence [2,2] also contains the whole singular scroll; it is produced by the points of its intersection with  $V$ .

§ 4. *a. Image of a plane curve  $r^n$  (in the plane  $V$  with nullpoint  $N$ ).* This intersects  $V$  along  $r^n$  and along the  $2n$  rays of the plane pencil  $(N, V)$  that are the images of the points  $(r^n, k_V^2)$ . It is accordingly a scroll  $R^{3n}$  with  $r^n$  as directrix and with  $5n$  singular rays among its generatrices owing to the  $5n$  points of intersection  $(r^n, R_s^5)$ . The nodal curve of  $R^{3n}$  passes through the  $2n(n-1)$  points of intersection of  $r^n$  with the generatrices through  $N$  in so far as they do not lie on  $k_V^2$ .

*b. Image of a twisted curve  $\varrho^n$ .* The congruence  $(u, \nu)$  of  $L$  has as image an  $O^3$ . To the  $3n$  points  $(\varrho^n, O^3)$  correspond  $3n$  rays, that rest

on  $u$  and have their images on  $\varrho^n$ . The image scroll is accordingly an  $R^{3n}$ . Among the generatrices there are  $5n$  singular rays corresponding to the points  $(\varrho^n, R_s^5)$ .

c. Image of a scroll  $R^n$ . This is found through inversion of  $b$ . The image curve  $\varrho^x$  has as image an  $R^{3x}$  but also  $R^n$  completed by the null planes of the  $5n$  singular points  $(R^n, \delta_s^5)$  that lie on  $\varrho^x$ . Hence:  $3x = n + 5n$ , consequently  $\varrho^x = \varrho^{2n}$ .

Also directly in the following way:  $\varrho^x$  cuts a plane in as many points as there are rays common to  $R^n$  and the congruence  $[2, 2]$  which represents the points of  $V$ . And for this number we find  $2n$ .

§ 5. a. Image of a surface  $O^n$ . As  $O^n$  cuts the conic  $k^2$  of an arbitrary point in  $2n$  points and also the  $k^2$  of an arbitrary plane, the image congruence is a  $[2n, 2n]$ . Any generatrix of  $R_s^5$  has  $n$  points in common with  $O^n$  so that the singular scroll, counted  $n$  times, belongs to the  $[2n, 2n]$ . Further  $5n$  plane pencils of the congruence correspond to the points  $(O^n, \delta_s^5)$ .

b. Image of a  $[p, p]$  of  $L$ . Let this be a surface  $O^x$ . This passes through  $\delta_s^5$  with  $p$  leaves because in any point of the singular curve  $p$  rays of the  $[p, p]$  are represented. Now inversely the image of  $O^x$  is a  $[2x, 2x]$ , but also the  $[p, p]$  completed by  $p$  times the congruence  $[5, 5]$  which consists of all the complex-plane pencils with nullpoints on  $\delta_s^5$ . This leads to the equation  $2x = p + 5p$ , hence  $O^x = O^{3p}$ .

§ 6. A straight line  $u$  that contains 3 singular points, is a (singular) ray, as otherwise the scroll  $R_u^3$  which represents the points of  $u$ , would be of an order higher than 3. Inversely a singular ray  $u$  always contains 3 singular points for if this number were more or less the order of  $R_u^3$  would be too high or too low; in other words:  $u$  is a trisecant of  $\delta_s^5$ . Hence  $R_s^5$  is the scroll of the trisecants of  $\delta_s^5$ .

For this reason  $\delta_s^5$  cannot be a rational curve. For this would have a surface of trisecants of the order 8. The singular curve is of the genus 1. This appears as follows. The nets of rays  $(u, v)$  and  $(w, x)$  out of  $L$  have as images cubic surfaces  $O_u^3$  and  $O_w^3$ , which cut each other along  $\delta_s^5$  and along a  $\varrho^4$  on which the scroll  $R^2 = (u, v, w)$  is represented which is common to the two congruences  $[1, 1]$ . The generatrices of  $R^2$  which belong to the nets, are unisecants of  $\varrho^4$  for all the representations in question. Such a generatrix can only have its image point in common with  $\varrho^4$  as it is not cut by any other straight line of the same kind and consequently cannot contain any other image. The other system of straight lines on  $R^2$  consists, accordingly, of trisecants of  $\varrho^4$  and this curve is, therefore, rational; the number of its apparent double points is 3.

Now the theory of the intersection of 2 algebraic surfaces  $O^m$  and  $O^n$  of which the intersection  $\varrho^{mn}$  consists of a  $\varrho^p$  and a  $\varrho^q$ , teaches that:

$$h_{pq} + 2h_q = q(m-1)(n-1).$$

$h_{pq}$  is the number of straight lines through a point  $P$  which have one point in common with  $\varrho^p$  and another with  $\varrho^q$  and  $h_q$  is the number of chords of  $\varrho^q$  through  $P$ .

We apply this to  $\varrho^9 = (O_u^3, O_w^3) = \varrho^4 + \delta_s^5$ . Now  $h_{pq} = 10$ , for although the cones  $(P, \varrho^4)$  and  $(P, \delta_s^5)$  have 20 generatrices in common, 10 of them do not cut  $\varrho^4$  and  $\delta_s^5$  in different points for  $\varrho^4$  contains the 10 points  $(R^2, \delta_s^5)$ . Further  $q = 5$ ,  $m = n = 3$ , so that the above mentioned equation gives:  $10 + 2h_q = 5(3-1)(3-1)$ , consequently  $h_q = 5$ , hence  $\delta_s^5$  is of the genus 1.

It is in accordance with this that we can pass  $\infty^4$  cubic surfaces through  $\delta_s^5$ . For the complex contains  $\infty^4$  nets  $(u, v)$  and each of them has its own image  $O^3$  through  $\delta_s^5$ . The condition that  $O^3$  must pass through  $\delta_s^5$  is accordingly 15-fold.

§ 7. Also several properties regarding degeneration of image figures hold good for all the representations in question, e. g.: there exists a complex of the fifth order of lines  $u$  for which  $R_u^3$  degenerates into a scroll and a plane; this complex contains all the lines that rest on  $\delta_s^5$  and has, therefore, this curve as locus of the cardinal points. A congruence [5, 10] belongs to it which consists of the chords of the singular curve which contains lines  $u$  for which  $R_u^3$  degenerates into a triple of planes one of which passes through  $u$ . To this congruence there belongs again the singular scroll for the generatrices of which  $R_u^3$  degenerates into 3 planes through  $u$ . As a locus of points  $R_s^5$  is the set of the vertices of all the plane pencils with degenerate image-conics  $k^2$ , the non-singular components of these pairs of lines form the above mentioned congruence [5, 10].

§ 8. The singular figures themselves can also degenerate. This will appear from a few examples which serve at the same time as a check on the above.

a. Suppose a fixed plane  $a$  and in it 2 projective pencils  $(F_1, a)$  and  $(F_2, a)$ ; further a fixed straight line  $a$  through  $F_2$  outside  $a$ . A ray  $s$  of  $L$  cuts one ray  $t_1$  of  $(F_1, a)$ . Associated to this is  $t_2$  of  $(F_2, a)$ . Put  $\mu = (a, t_2)$  and take  $S = (\mu, s)$  as image of  $s$ . Inversely we can find the image ray of a point  $S$  through the following construction:  $\mu = (a, S)$ ;  $t_2 = (\mu, a)$ ;  $t_2$  gives the homologous ray  $t_1$  of  $(F_1, a)$ ;  $T = (v, t_1)$ , where  $v$  is the null-plane of  $S$ ;  $s = ST$ .

b. If  $S$  is a point of  $a$ ,  $\mu$  is indefinite; also  $t_2$  and, accordingly,  $t_1$ , so that  $T$  becomes any point of  $(v, a)$  and  $s$  any ray of  $(S, v)$ . In other words: all the points of  $a$  are singular points.

The projective pencils in  $a$  produce a conic  $a^2$  through  $F_1$  and  $F_2$ . A point  $S$  on it defines a definite plane  $\mu = (S, a)$ , hence also definite lines  $t_2$  and  $t_1$ , but  $T = (v, t_1) \equiv S$ , so that for  $s$  we may choose any ray of the plane pencil  $(S, v)$ :  $a^2$  is another part of the locus of the singular points.

Let  $t_1$ ,  $t_2$  and  $\mu$  have the usual meaning. Let  $\beta$  be the nullplane of  $F_1$ ; this passes through  $A$ , the nullpoint of  $a$ .  $\beta$  contains  $p_1$  through  $A$ , the directrix of  $L$  associated to  $t_1$ , and  $p_2 = (\mu, \beta)$ . Consider  $S = (p_1, p_2)$ , which lies in  $\mu$ . The null plane  $\nu$  of  $S$  passes through  $t_1$ ; the point of intersection  $(\nu, t_1)$  is, therefore, indefinite; consequently  $S$  is a singular point. Owing to the correspondence (1,1) between the plane pencils  $(p_1)$  and  $(p_2)$ , the locus of  $S$  is a conic  $b^2$  in  $\beta$  through  $A$  and  $B = (a, \beta)$ . Let  $C$  be the second point of intersection of  $AF_1$  with  $a^2$  and choose  $p_1 = AC$ . Then  $t_1 = AC$ , because  $AC$  belongs to  $L$ . Further  $t_2 = F_2C$  and  $p_2 = BC$ , hence  $S = C$ . Consequently the conics  $a^2$  and  $b^2$  cut each other in  $C$ .

Suppose that  $P$  outside  $a$ ,  $a^2$  and  $b^2$  is a singular point. The cones  $(P, a^2)$  and  $(P, b^2)$  have 3 generatrices in common besides  $PC$ , which of course do not lie in one plane. But according to § 6 they must nevertheless be (singular) complex-rays. Hence  $P$  is not a singular point. The locus of the singular points is  $a + a^2 + b^2$ , a degenerate  $\delta_2^5$ ; it has 5 apparent double points. For the cones  $(P, a^2)$  and  $(P, b^2)$  have three generatrices in common which rest on  $a^2$  and  $b^2$  in two different points; and the plane  $(P, a)$  cuts each of these cones besides along  $PF_2$ , resp.  $PB$ , along one generatrix in 2 non-coinciding points.

c. A ray of  $(F_1, \beta)$  cuts all the rays  $t_1$  (in  $F_1$ );  $t_1, t_2$  and  $\mu$  are therefore, indefinite, hence also  $S = (\mu, s)$ . The same holds good for the rays of  $(A, a)$ , for these also cut all the  $t_1$ . The scroll which has  $a$ ,  $a^2$  and  $b^2$  as directrices, is of the third order:  $R_s^3$ . Each of the generatrices of  $R_s^3$  contains 3 singular points and is, therefore, a singular ray.

Accordingly we have found a figure of the fifth order,  $R_s^5 = a + \beta + R_s^3$ , which consists of such rays. That this is the locus of these rays appears e.g. in the following way: let  $s$  be a singular ray which does not belong to  $R_s^3$ ; its intersection  $S$  with  $a$  is the image of  $s$  and  $SA$  and would, therefore, be a singular point; but  $a$  does not contain any such a point outside  $a^2$ .

As it should be  $a + a^2 + b^2$  appears to be the nodal curve of  $a + \beta + R_s^3$ .

§ 9. Another possible degeneration of  $\delta_s^5$  is: 2 crossing straight lines ( $a$  and  $a_1$ ) with a transversal ( $a_2$ ) and a conic ( $b^2$ ) which cuts the former two lines. This happens in the representation through 2 projective plane pencils if we choose them in perspective correspondence. In this case  $a^2$  degenerates into  $a_2 = F_1F_2$  and the axis of perspectivity  $a_1$ , which continues to have a point  $C$  in common with  $F_1A$  through which  $b^2$  also passes. The singular surface  $(R_s^5)$  consists of the planes  $\alpha, \beta$  and  $(a, a_2)$  and the scroll that has  $a, a_1$  and  $b^2$  as directrices.

We can also establish a perspective correspondence between the plane pencils  $(A, \beta)$  and  $(B, \beta)$ . For this it is only necessary that we associate the directrix of  $L$  corresponding to  $AB$  as homologous ray to the ray  $AF_2$  of the plane pencil  $(F_2, a)$ .

Finally we can transform both projectivities into perspective correspondences, through which  $\delta_s^5$  is transformed into a skew pentagon. Instead of  $b^2$  we find  $b_1 = AB$  and a straight line  $b_2$  cutting  $b_1$  and cutting  $a_1$  in  $C$ .  $R_s^5$  has degenerated into 5 planes  $(a, b_1)$ ,  $(b_1, b_2)$ ,  $(b_2, a_1)$ ,  $(a_1, a_2)$  and  $(a_2, a)$ .

It is easily seen that for the latter degenerations the number of apparent double points is again 5 and that  $R_s^5$  has the curve  $\delta_s^5$  as nodal curve.

A very special case is  $F = F_1 = F_2$ . In this case we have 2 collocal projective plane pencils; we may also use an involution of rays. Geometrically it is easily seen that again the fixed straight line  $a$  and a conic  $b^2$  in the null plane  $\beta$  of  $F$  (quite analogous to the homonymous plane of § 8 b), belong to the singular points, and that  $a + b^2$  is completed to a  $\delta_s^5$  by the rays of coincidence  $c_1$  and  $c_2$ . It appears as above that the complex pencils in  $\beta$  and in  $\alpha = (c_1, c_2)$  consist of singular rays.

The cubic scroll  $R_s^3$  splits up into the planes  $(a, c_1)$ ,  $(a, c_2)$  and  $\beta$ .

Accordingly the null plane  $\beta$  of  $F$  must be considered as a double plane in the locus of singular rays and, therefore, an arbitrary point of  $\delta_s^5 = a + b^2 + c_1 + c_2$  is again the point of issue for 2 singular rays. As  $b^2$  appears to pass through the null points of  $\alpha$ ,  $\beta$ ,  $(a, c_1)$  and  $(a, c_2)$ , all these rays are again trisecants of  $\delta_s^5$ .

§ 10. Also each of the other forms of degeneration of the singular curve has its own singular scroll, degenerate or not, which may always be derived from it through the relation:  $R_s^5 = \text{surface of trisecants of } \delta_s^5$ .

a.  $\delta_s^5 = \text{rational } \delta^4 + \text{chord } k$ .

The singular scroll consists of the scroll of trisecants of  $\delta^4$  and the scroll formed by the chords of  $\delta^4$  through the points of  $k$ ; it is easily seen that this surface is of the third order and has  $k$  as a nodal line.

b.  $\delta_s^5 = \text{non-rational } \delta^4 + \text{unisecant } k$ .

In this case the surface  $R_s^5$  is not degenerate: it consists of the chords of  $\delta^4$  that rest on  $k$ . Besides the line  $k$ , counted double, the intersection with a plane  $V$  through  $k$  contains 3 more chords of  $\delta^4$  through 3 singular points, namely the joints of the 3 points  $(V, \delta^4)$  outside  $k$ ; accordingly this intersection is indeed of the fifth order.

c.  $\delta_s^5 = \delta^3 + \delta^2$ ;  $\delta^3$  and  $\delta^2$  have 2 points in common.

$R_s^5$  consists of the pencil in the plane of  $\delta^2$  with vertex in the point where this plane is cut by  $\delta^3$  outside  $\delta^2$ , and of a scroll of the fourth order consisting of the chords of  $\delta^3$  that rest on  $\delta^2$ .

This is the case with a few representations of  $L$  found by professor JAN DE VRIES, e. g.:

A ray  $s$  cuts the fixed plane  $a$  in  $P$ ; let  $p$  be the polar line of  $P$  relative to a given conic  $a^2$  in  $a$ ,  $\rho$  the plane through  $p$  and a fixed point  $C$ ;  $S = (s, \rho)$  is chosen as the image of  $s$ . Inversely the image ray of a point  $S$  is found by choosing that ray of the null plane of  $S$  which

rests on the polar line  $q$  of  $Q$  relative to  $a^2$ , if  $Q$  is the intersection of  $CS$  and  $a$ .

It is at once clear that the complex plane pencil  $(A, a)$  consists of singular rays and  $a^2$  of singular points. We find further that at any point of  $a^2$  one tangent to the cone  $(C, a^2)$  may be drawn which belongs to  $L$  and does not yield any definite point  $S$  because  $q$  passes through it. Closer examination shows that this kind of singular rays forms a surface of the fourth order with nodal curve  $\delta^3$  which passes through  $A$  and through the points where  $a^2$  is touched by the tangents through  $A$ . In this way the aforesaid is justified.

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