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(Communicated in the meeting of October 29, 1910).

Since the appearance of our first paper on the temperature optimum of physiological processes, [1]) a communication was published by Mr. A. A. L. RUTGERS [2]) "Influence of temperature on the geotropic praesentation time of Avena sativa".

Beside the discussion of the highly interesting and accurate observations concerning the said subject, this paper gives a comparison of the results obtained by Mr. RUTGERS with those of other experimenters, and our paper, referred to above, is more specially submitted to criticism in it. Considering that the detailed record of the values on which our preliminary publication is based may still stay out some time, we thought it desirable already now to vindicate the conclusions which we have drawn from our results against the objections advanced by Mr. RUTGERS. At the same time we use this opportunity to indicate some new considerations in support of our views.

It may be called to mind that we had studied the relation between temperature and fermentation velocity, such as it appears after mixing a yeast suspension with an excess of glucose solution and after the so-called "Antrieb" is past [3]). Thereby it was found that in contradiction with what after the theory of DUCLAUX-BLACKMAN might have been expected, already before a lasting noxious influence of the temperature on the fermentation function becomes perceptible a distinct deviation from the rule of VAN 'T HOFF sets in, which is even so great that the velocity-temperature-curve changes in respect to the temperature axe from convex to concave.

For different fore-heating periods (5, 10, 15 and 20 minutes) one and the same curve for the relation between velocity and temperature was found, as might be expected à priori. At noxious temperatures this relation for the 4 mentioned times of fore-heating is also represented by 4 different curves, and by now stating at a determined time of foreheating and a determined temperature what part of the yeast

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[1]) These Proceedings June 25, 1910 p. 227.

[2]) These proceedings Oct. 29, 1910 p. 476. In Mr. RUTGERS' Dissertation the same subject is treated elaborately.

[3]) For the sake of simplicity we leave out for the moment the inversion of cane sugar, which was studied by us in a corresponding way.

has lost the function, it was possible from each of these 4 curves to calculate the curve which would have occurred if the temperature had not exerted a (lasting) noxious influence. Indeed, by these 4 ways was actually obtained the same curve, showing a pronounced optimum and forming the continuation of the simple curve found for harmless temperatures for the 4 fore-heating periods. It should besides be noticed that also the velocities above the noxious temperature were first measured after the "Antrieb" was finished, which proved to be the case when about 20 cM³ CO_2 had evolved.

We think that from these results the conclusion must be drawn that the theory of DUCLAUX-BLACKMAN should be rejected, for after this theory, when no injury of the active agent by the high temperature was occasioned, the relation between velocity and temperature would be represented by a continuously rising curve, and its growing concave beneath, as well as its falling above the optimum would be caused by the injury of the active agent during the fore-heating.

Against this conclusion now Mr. RUTGERS advances in the first place the following:

In his researches the praesentation time wanted for the perception of the gravity by coleoptiles of oat-germplants for temperatures of 0°, 5°, 10°, 20°, and 25° C. proved to be independent of the time of fore-heating (the successive fore-heating periods differed at least 1 hour from each other). At 30° C., however, the praesentation time proved to *decrease* with the time of fore-heating; after about 12 hours, the shortest praesentation time was attained which, after 24 hour's fore-heating was still maintained. On the other hand, above 30° the praesentation time *increased* with continuation of the fore-heating: at 35° C. it attained a maximum after 18 hours, which it had still preserved. after 24 hours; at 37° and 38° C. however, it increased continuously, as long as the fore-heating was continued to 24 hours).

We should bear in mind that the praesentation time cannot be compared with the velocity of a process, but to a certain extent to the reciprocal value of a velocity. So the curve "praesentation time-temperature" shows a "temperature minimum" (with a slight difference only for the different periods) of fore-heating instead of a "temperature optimum".

From the fact that at 30° C. at first a greater value for the praesentation time is found, which decreases with continuation of foreheating, RUTGERS concludes that the higher temperature only reaches its full favorable influence after a prolonged remaining at that temperature, and on the ground of the literature thereabout he thinks this must be considered as a common phenomenon.

That at temperatures above 30° with continued fore-heating an *increase* of the praesentation time is obtained, should now, according to Rutgers, be ascribed to the fact that the favourable action of the continued fore-heating is quite annulled by the noxious influence arising at the same time. Such a noxious action might, according to Rutgers, in his experiments already be active at 30° C., but there the favouring by continued fore-heating would be greater than the injury. Rutgers thinks this must be concluded from the fact that the curve, found by him by extrapolation for a time 0 of fore-heating, at 30°, indicates a lower value of the praesentation time than that practically found after 1 hour's fore-heating.

If now it is right that also at higher temperature than 30° a favouring influence by continuation of the fore-heating may be admitted, the values found for the praesentation times after 1 hour, 2 hours, etc. of fore-heating, would, without that favourable action, be higher than they are now.

After Rutgers it is on this account not allowed to draw conclusions after different times of fore-heating about the praesentation time or the velocity of a physiological reaction (indifferently whether this is done by calculation as in our method or by extrapolation as in that followed by Blackman and others), if no account is kept with the favourable influence of continued fore-heating. He thinks that if this is done, Blackman's theory for the explanation of the temperature-optimum proves to be right and that for the relation between temperature and praesentation time, resp. the velocity of the reaction at a fore-heating time of 0, a curve without minimum resp. optimum will be found.

It may be remarked here at once that Rutgers has not confirmed by observations this modified theory of Blackman. For this a special study of the noxious influence by continued fore-heating would have been required and sufficient; such a study, however, has not been made and hence, the testing of his theory with his own results is impossible.

Mr. Rutgers has thus only pointed to the "possibility" that this modified theory of Blackman might give an explanation of the phenomena.

We now wish to prove that this modified theory is not confirmed by *our* observations, without the support of new accessory hypotheses.

To this end we state that, according to Rutgers, the considerable deviations from the rule of van 't Hoff, too, may be explained by the fact that hereby likewise favourable and injurious influences of continued fore-heating would appear side by side.

Could the favourable influence be eliminated we should, in accordance with this view, by our observations, already below 45° have found four different curves for the four different periods of fore-heating, and the zero-curve calculated herefrom or found by extrapolation, would have answered VAN 'T HOFF's rule. That we now only found one single curve might be explained by the circumstance that here the favouring influence annuls the noxious. Now it is in itself already an adventurous supposition, that at the 4 different periods of fore-heating those two influences always annul each other, but its possibility is not excluded. However, the fact should be emphatically pointed out that a *lasting* noxious action on the yeast at those temperatures at which the curve is simple was not observed during the time of our experiments: when the yeast, after being heated for 20 minutes at 45° C., was cooled to 20° C., it showed the same fermentation velocity as if no heating had taken place. Yet, in order to accept BLACKMAN's theory, it should be admitted that at the fore-heating ± 35 °/₀ of the yeast had lost its activity.

Now, here again an outlet might be found by introducing a second new hypothesis. It might be admitted that the inactivation of the fermentation function had taken place "invertibly", but then it must also be admitted that for the inactivation at temperatures at which the single optimum curve must be replaced by many, an uninvertible annihilation exists together with the invertible inactivation. Moreover, then still the fact remained to explain that the 4 optimum curves for the time 0, which we calculated from the different curves observed at noxious temperatures, only taking the "lasting" noxious action, into account, fall together into one. Neither this is to be conceived without the help of a third hypothesis, for, if this holds good for the 4 zero-curves found after RUTGERS' calculation this will not in general be so with the curves calculated after our method.

These three new hypotheses should moreover not only be accepted as valid for the alcohol fermentation, but also for the inversion action of cane sugar.

Let us now consider the fundamental assumption whereon this part of RUTGERS' opposition is based. After his view a favourable influence increasing with the time of fore-heating might also in our experiments have been of some weight.

We think, however, the motives for this conception insufficient. For it reposes in the first place on a conclusion derived by this experimenter from modifications stated in the praesentation time for

30°, and fore-heating times of from 1 to 24 hours, and, further on the consideration that we were always obliged to let an "Antrieb" pass before we obtained constant values of the fermentation velocity. In the first place, now, we do not think the comparison of his experiments with ours justified: our longest fore-heating times lasted 20 minutes, of adaptation or growth phenomena there is hardly question in so short a time whereas such processes will no doubt occur in the long periods of RUTGERS' experiments[1]). We even see in this circumstance the probable explanation of the differences in the course of the curves obtained by him for the relation between praesentation time and time of fore-heating at a temperature of 30° and higher.

Moreover, even if we accepted a favourable influence, by continued fore-heating, as vigorous as was observed in this experiment of RUTGERS, that influence, during 20 minutes, i.e. our longest time of fore-heating, would not have been of much importance. For in the 20 minutes which succeed the hour of fore-heating in his experiments, the praesentation time changes only from 210″ to 217″, a modification falling within the limits of observation errors.

Furthermore, the rising of the fermentation velocity during the "Antrieb" must by no means be exclusively ascribed to the action of the continued fore-heating: an "Antrieb" also originates without heating. Hereby a number of factors will play a part: so, with our method of working, the glucose solution did not immediately penetrate into the cells. In fact, all kinds of experimental mistakes accumulate in this factor.

We do not, however, intend to neglect the here meant time factor; it is quite certain that first the "Antrieb" must be finished before the temperature is able to exert its full influence.

Let us therefore consider the significance of this factor with reference to the table below, which relates to special experiments performed for the study of that factor.

It is clear that this table gives but a very imperfect image of the rate of velocity during the "Antrieb". What will be the initial velocity at the beginning of that "Antrieb"; to this we shall certainly get no satisfactory answer based on these experiments[2]). It

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[1]) Compare here in particular the Dissertation of Mr. RUTGERS.

[2]) Supposed that this "initial" velocity proved to have the value 0 (and to this our results do point), or that it was perfectly constant for all temperatures (for instance that of 20° C., as may be expected at another arrangement of the experiments), what, then, remains of the determination of a temperature curve for *that* initial velocity?

Fermentation velocity in cM³. CO_2, evolved per second.

cM³. CO_2.	40 grs. yeast 78½ cM³. H_2O 25 cM³. gluc. sol. temp. 40°.	12 grs. yeast 32.8 cM³. H_2O 10 cM³. gluc. sol. temp. 45°.	6 grs. yeast 34.8 cM³. H_2O 10 cM³. gluc sol. temp. 45°.	16 grs. yeast 31.4 cM³. H_2O 10 cM³. gluc. solution temp. 45°.	
0—5	0.152	0.135	0.106	0.157	0.179
5—10	0.250	0.209	0.144	0.250	0.262
10—15	0.357	0.253	0.190	0.312	0.333
15—20	0.417	0.333	0.190	0.357	0.385
20—25	0.500	0.357	0.200	0.333	0.419
25—30	0.625	0.333	0.208	0.385	0.417
30—35	0.625	0.357	0.208	0.357	0.357
35—40	0.625	0.333	0.200	0.385	0.357
40—45	0.625	0.312	0.208	0.417	0.385
45—50	0.625	0.333	0.200	0.417	0.417
50—55		0.333	0.200	0.417	0.417
55—60		0.333	0.208	0.454	0.455
60—65				0.417	0.417

seems however, that we can get out of this difficulty by an other way.

For all non-lasting-noxious temperatures the fermentation velocity — and after our experience the same holds good for very different physiological processes [1] — attains after a relatively short period in which an irregular rate is observed, a constant value which is maintained much longer than the first irregular course. That constant value, now, proves at a fixed regulation of the circumstances which govern the process, exclusively dependent on the temperature. Hence it is evident that the relation should be sought between *that* velocity, and the temperature and to fix for that velocity the temperature-

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[1] It is a fact that also for physico chemical reactions a certain time must be allowed to pass before the process proceeds with the theoretically expected velocity. This is particularly obvious in photo chemical processes: not before the end of the so-called "photo-chemical induction time" the quantity of converted matter becomes proportional to the product of time and light intensity (compare for instance **Nernst**, Theor. Chemie, 2 Aufl., S 603). Now, certainly nobody when studying the temperature-coefficient of the photo-chemical process, will be desirous to trace the initial velocity existing at the beginning of that induction time.

curve; then the question rises whether with exclusion of noxious influence by high temperature, the temperature-curve would either or not show an optimum.

Such was the problem proposed in our paper and the result was that without a noxious influence still an optimum curve was found. Were it possible to heat the yeast without injury it would be evident that the constant fermentation velocity, setting in after the "Antrieb" is past, reaches an optimum for a certain temperature.

A second objection is advanced by Mr. RUTGERS against our conclusions. In our paper we called to mind that beneath (lasting) noxious temperatures considerable deviations from VAN 'T HOFF's rule appear and in our opinion the theory of BLACKMAN should already be rejected on that account.

As an explanation for our results RUTGERS now suggests the possibility that the diffusion velocity through the cell-wall may have acted in our experiments as a limiting factor in the sense of BLACKMAN's theory. To this we observe in the first place that there is much more reason to suppose this factor playing a part in the experiments of KUYPER and BLACKMAN on the respiration and carbonic acid assimilation of higher plants, wherewith these investigations kept no account.

We think, however, that for the fermentation it must be admitted that the diffusion through the wall of the yeast cells does not restrict the fermentation velocity. Supposing that sugar diffuses through the wall with a velocity only 10^{-3} times as great as the diffusion velocity in water, then a calculation, which we hope to give later, proves that more than 10^3 times as much glucose may enter through the wall as was maximally fermented in our experiments.

Moreover, if RUTGERS' supposition was right, our curve beneath the optimum would represent the relation between the quantity of the matter diffusing through the wall and the temperature, while it is known that this relation is represented by quite another curve. ¹)

Certainly the possibility exists that to explain an optimum — also in absence of injurious influence by the heating — some limiting factor must be taken in consideration. But this can certainly not save the theory of BLACKMAN to explain the occurrence of that optimum. For the bent of the velocity-temperature curve is, according to that hypothesis, solely to be attributed to dying of the function at the fore-heating, consequently to the time factor.

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¹) Compare for instance WÜLLNER, Experimental Physik, Bd. I, S. 456.

Here we wish still emphatically to point out that it has never been our intention to underrate the great signification of the introduction of the conception "limiting factors" by BLACKMAN; what by this investigator has in general been observed about this point, preserves its full vigour, also when accepting our conclusions.

A third objection which Mr. RUTGERS brings forwards against our views as to the course of the temperature curve beneath the optimum, is that also at various common chemical reactions quite analogous deviations from the rule of VAN 'T HOFF have been stated. We think, however, that this well-known fact must not be advanced against our conclusion. For, admitting that for physiological processes, also at harmless temperatures, the rule of VAN 'T HOFF is of no consequence what then remains of BLACKMAN's theory?

For in this case there is not the least objection to suppose that also in absence of noxious influences the value of the temperature coefficient lowers to 0 or even becomes negative. Even some physicochemical processes are known which proceed with a decided temperature optimum. So, the number of crystal germs produced at different temperatures in undercooled solutions, as TAMMANN's [1]) researches prove. The most remarkable results in this respect are those of C. ERNST, whereby the relation between the velocity of the catalysis of hydro-oxygen by colloidal platinum is described. For this catalytic process, which exhibits in many respects interesting analogies with physiological processes, ERNST comes to the result that beneath a certain temperature, for different times of fore-heating one single curve is found for the relation: reaction-velocity-temperature, whilst besides, with different fore-heating times, also different curves are found.

He further shows that fore-heating at higher temperatures causes a (lasting) noxious influence on the reaction velocity, which injury he also determines after the method followed by us. When now he calculates the curve: velocity-temperature for a fore-heating time 0, he also obtains a curve showing an optimum. The results obtained by this anorganic process are thus quite in accordance with those found by our experiments.

It must still be remarked that during the time taken by his experiments performed to observe the temperature optimum (with fore-heating periods of 4 and 5 hours), ERNST did not detect a favourable influence by continued fore-heating. A slight decrease of velocity, hardly perceptible after 4 days, but after 14 days somewhat visible, found

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[1]) Zeitschr. f. Phys. Chem. Bd. 25, 1898, S. 441.

its explanation wholly in the change of the concentration during the reaction.

Here also Mr. Rutgers is obliged, if he wishes to maintain the favourable influence, to admit an "invertible" noxious action, which levels that very influence.

To be sure we should by no means wish to omit mentioning that under the greatest possible reserve Ernst gives an explanation for the occurrence of the optimum curve in absence of injury, whereby this curve is again represented as the resultant of a rising and a descending curve. But the factor rising with the temperature as well as that falling with it, would according to Ernst, be of quite another nature than the factors which play a part in the theory of Duclaux-Blackman. For the increasing of the reaction-velocity with rise of temperature must in his opinion be a consequence of the greater value of "absorption velocity" at higher temperature; the decrease should be ascribed to the reduction of the quantity of the gas absorbed by the platinum surface at such a temperature. Of the before mentioned *time factor* there is no question here whereas in Duclaux-Blackman's theory the decrease should exclusively be ascribed to it.

Referring to the preceding we still wish expressly to state that Mr. Rutgers is quite wrong in presuming that it would be our intention to contest Blackman's view, "that for explaining the reaction-velocities on botanical territory the physico-chemical laws must be the real base". (See page 154 of his Dissertation). If one wishes for example, to compare our optimum curve, occurring when no noxious action is present, with the reaction curve for the process studied by Ernst, there is of course not the least objection. In our opinion it may be expected that specially the investigation of coagulation phenomena of proteids under the influence of temperature on one hand, and that of adsorption phenomena on the other, will give an explanation for the origin of such a curve.

Summarising we come to the following conclusions:

1. The theory of Duclaux-Blackman to explain the occurrence of an optimum temperature is not accepted unmodified by Rutgers.

2. That it is confirmed by the facts, when modified as proposed, has not been proved by Rutgers.

3. Results found by us for physiological processes can only be brought into accordance with the modified theory by introducing three new hypotheses. For none of these efficacious arguments can be given.

4. For the study of the relation between reaction velocity and

temperature one has to take the (practically) constant velocity, which, when the experiment is rightly performed, sets in after a short period.

5. The thus studied velocity shows also in absence of (lasting) noxious influences, an optimum for a certain temperature, which is contrary to the theory of Duclaux-Blackman for the explanation of the occurrence of a temperature optimum at physiological experiments, this theory should hence be rejected.

6. The diffusion through the wall of the yeast cells is no limiting factor in the processes studied by us.

7. The fact that also physico-chemical reactions deviate from the rule of Van 't Hoff cannot be opposed to our conclusion that, in the case of the alcohol fermentation, the considerable deviation from that rule beneath noxious temperatures is in contradiction with the theory of Duclaux-Blackman.

8. On the contrary, it speaks greatly in favour of our observations and conclusions that the catalysis of hydro-oxygen-mixtures by colloïdal platinum (which process presents also in other respects much analogy to physiological katabolisms) shows a temperature optimum in absence of (lasting) noxious action, so on exclusion of the time factor, and behaves with respect to the temperature perfectly in the same way as was found by us for the alcohol fermentation and the inversion of cane sugar by yeast invertase.

Delft, October 1910.

Physics. — "*Isotherms of monatomic gases and of their binary mixtures.* VI. *Coexisting liquid and vapour densities of argon; calculation of the critical density of argon.*" By C. A. Crommelin. Comm. N°. 118[1] from the Physical Laboratory at Leiden. (Communicated by Prof. H. Kamerlingh Onnes.)

(Communicated in the meeting of September 24, 1910).

§ 1. The experiments published a short time ago[1]) by which the vapour pressures of argon above — 140° C. were determined afford a means of deriving the difference between the coexisting liquid and vapour densities at the same temperatures as those at which the vapour pressures were measured. As was mentioned in § 2 and 3 of the paper just referred to, both the position of the argon meniscus in the low temperature reservoir and that of the mercury meniscus

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[1]) These Proceedings May 1910. Comm. Phys. Lab. Leiden, N°. 115. For short, this paper which is frequently quoted in the text will be called Comm. 115.

in the stem of the piezometer (immersed in a water bath at about 20° C.) were read off in the two measurements that formed each vapour pressure determination. As the cross-sections of the reservoir and of the piezometer stem were known and the temperature of the waterbath was noted, and as, moreover, the density of the gaseous argon in the stem could be calculated from argon isotherms which will soon be published by Prof. KAMERLINGH ONNES and myself[1]), all the data necessary for the calculation of the difference between the liquid and vapour densities were known. For the mass of the gas by which the quantity in the stem has been lessened during condensation is equal to the mass of liquid formed *minus* the mass of saturated vapour that at the beginning of condensation occupied the space taken up at the end of condensation by the liquid that has been formed. In the calculation a correction has been made for the volume of the glass stirrer in the low temperature reservoir

§ 2. The *results* lay no claim to an accuracy equal to that of the vapour pressure determinations in the paper referred to. The accuracy can be estimated at from 1 to 1½ %, but the fact that nothing is known concerning the liquid and vapour densities of argon in the region covered by my experiments seemed to me to justify the publication of these results. The calculations (in which, of course, allowance was made for the small impurity in the argon) could be made only for series VI, V, III, and IV, and II of Comm. 115, since the temperature in the two series VIII and IX was in the immediate neighbourhood of the critical temperature, and the meniscus was too unsteady to allow of fairly sharp readings.

The results obtained are collected in the following table. As usual the subscripts 1 and 2 refer to the liquid and vapour states respectively; the densities are given with respect to water at 4° C.

Date	Series	t	p [2])	$d_1 - d_2$
1910. 10 Febr.	VI	—140.80	22.185	0.9195
10 »	V	—134.72	29.264	7718
9 »	III and IV	—129.83	35.846	6502
9 »	II	—125.49	42.457	4714

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[1]) In the present paper frequent use is made of these isotherms.

[2]) For the sake of completeness vapour pressures (already published in Comm. 115) are here inserted in the table.

§ 3. *Deduction of the values of d_1 and d_2.* Now that $d_1 - d_2$ is known, the values of d_1 and d_2 may be reached by assuming that the CAILLETET and MATHIAS [1]) law of the rectilinear diameter holds for argon. Considering that the accuracy of the experiments with which we are at present concerned is not very great we may quite well base our calculations on this assumption, the more so as MATHIAS and KAMERLINGH ONNES [2]) have just shewn from very accurate measurements that oxygen obeys this law. The applicability of this law to argon, therefore, is not necessarily called into question by the fact that the critical temperature of argon is much lower than is the case with substances for which the validity of the law of the rectilinear diameter has been experimentally established.

To be able to apply this law, however, to our present purpose, we must know the data for the diameter with considerable accuracy. They can be deduced only very inaccurately from the liquid densities given by BALY and DONNAN [3]) which were used along with the diameter in Comm. 115 for determining the critical density. Their measurements, moreover, cover a range of only 6°, viz. from —189° C. to — 183° C. far removed from the critical temperature, and a difference of 0.2°/₀ between the errors in their extreme observations causes an error of about 3°/₀ in the critical density. And further, a small percentage error in the critical density is greatly magnified in the vapour volumes e. g. at — 130° C. about 4 times, at — 134° C. about 7 times and at — 140° C. about 13.5 times. When the values of d_1 and d_2 calculated from the estimate of d_k (0,496) based on BALY and DONNAN's results, which was used in Comm. 115, and the points on the boundary curve deduced from them were accordingly plotted in the pv-diagram of the argon isotherms and along with them experimental values of the vapour volumes obtained by slight extrapolation of accurate isotherms, it was seen that they deviated considerably from each other.

I tried therefore to obtain d_k independent of BALY and DONNAN with a view to finding the constants of the diameter from their liquid densities regarded as a determination of $d_1 + d_2$ for a single temperature far from the critical. This can be done with the help of the vapour pressures published in Comm. 115 and of the argon isotherms that are still to be published mentioned in § 1 of the present paper.

At the critical point the equation:

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[1]) L. CAILLETET and E. MATHIAS Journ. d. Phys. (2) 5, 549, 1886.

[2]) Zitt.versl. Juni 1910. C. R. Ac. d. Sc. Paris 151, 213 and 474, 1910.

[3]) E. C. C. BALY and F. G. DONNAN, Journ. Chem. Soc. 81, 911. 1902.

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{dp}{dT}\right)_{coex} {}^{1)} \quad \ldots \ldots \ldots \quad (A)$$

holds.

$\left(\frac{\partial p}{\partial T}\right)_v$ is with great approximation independent of temperature [2]; its values for successive densities in the neighbourhood of the critical density were read from a pv-graph of accurate isotherms just above the critical point. Hence these values hold, too, for the critical temperature itself. The value of $\left(\frac{dp}{dT}\right)_{coex.k}$ can be deduced from data published a short time ago [3]) viz: $\left(\frac{dp}{dT}\right)_{coex.k} = 1.820$. Interpolation between the values of $\left(\frac{\partial p}{\partial T}\right)_v$ obtained from the isotherms gave in this way 0.509 as the density for which equation (A) holds.

In connection with the deduction of this value, however, it must be remembered that this method has already led repeatedly to a result for d_k differing from that found from the diameter, and that the results obtained by the two methods deviate so far from each other that the difference cannot be attributed to errors of observation or calculation. The values obtained according to these two methods must therefore be regarded as experimental data differing in general from each other and each of them deduced in a certain way. For instance, KEESOM [4]) found 0.00418 for the experimental critical volume of carbon dioxide (expressed in the theoretical normal volume as unit) using the law of the diameter, and 0.00443 for the volume for which equation (A) holds. And KAMERLINGH ONNES and KEESOM [5]) mention that BRINKMAN [6]) found a similar difference in the case of carbon dioxide and of methyl chloride, as MILLS [7]) did for ethyl aether, isopentane and normal pentane. These deviations are such

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[1]) M. PLANCK, Ann. d. Phys. (4). 15. 457. 1882. KEESOM (Proc. Dec. 1901 Comm. 75) mentions three proofs communicated to him by Prof. VAN DER WAALS. One of them can be found in VAN DER WAALS—KOHNSTAMM, Lehrbuch der Thermodynamik. I, p. 35 and 36.

[2]) cf. W. H. KEESOM, Proc. Jan. 1904. Comm. N⁰. 88, (pg. 54). Thesis for the doctorate, Amsterdam 1904. p. 86.

[3]) Comm. 115, last page.

[4]) l. c.

[5]) Proc. Febr. 1908. Comm. N⁰. 104a, see also H. KAMERLINGH ONNES and Miss T. C. JOLLES. Proc. Febr. 1907, Suppl. 14.

[6]) C. H. BRINKMAN, Thesis for the doctorate, Amsterdam. 1904, p. 43.

[7]) MILLS, Journ. of phys. chem. 8. 594 and 635. 1904.

that the method of the diameter gives the smaller value for the critical volume. It was the deviation between the results obtained by these two methods that led KAMERLINGH ONNES and KEESOM to undertake the study of the disturbance function which must ascribe a mutual relationship to these and similar deviations. Until it shall appear that this is not the case with argon and it shall be found that the two values agree, as is not impossible for this substance, we must assume that the above value ($d_k = 0.509$) is smaller than that which would be given by an application of the diameter law to observations in the neighbourhood of the critical temperature, and this latter value is just the one that we require for our present calculations. In the meantime, however, there is no other course open to us than to base our calculations upon the value just given,

$$d_k = 0.509.$$

In this treatment of the question we neglect a difference which, if it could be considered equal to the differences usually existing between values of critical density as determined by these two methods would be much greater than that between the newly derived value and that used in Comm. 115 ($d_k = 0.496$).

As was mentioned in the beginning of this section a small change in the value of d_k is sufficient to cause a large alteration of vapour volume, and it is accordingly remarkable that a good agreement is obtained between the observed values and those calculated with the value of d_k now deduced. We must ascribe this to the fact that a value of d_k happens to have been found which is very suitable for the representation of coexisting liquid and vapour densities by the diameter, and this further leads us to suspect that the two methods of determining the critical density of argon will give results that differ but slightly from each other.

The calculations were made as follows: the diameter was drawn from the observations of BALY and DONNAN in the neighbourhood of the boiling point of argon using the above value of d_k, and the critical temperature lately published, — 122°.44 C. From the graph were read values of $^1/_2\ (d_1 + d_2)$ and from these and the observed values of $d_1 - d_2$, d_1 and d_2 were calculated. The results are given in the following table. For the sake of completeness there are also inserted in the table densities d_{A_1} and d_{A_2} in terms of the normal density (the wt. of 1 l. of argon = 1.782 g. under normal conditions according to RAMSAY and TRAVERS [1]) and volumes v_{A_1} and v_{A_2}, in

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[1] W. RAMSAY and M. W. TRAVERS, Proc. R. S. 67. 329. 1900.

terms of the normal volume; these volumes served along with vapour pressures known from Comm. 115 for the construction of the boundary curve in the *pv*-diagam.

Series	d_1	d_2	d_{A_1}	d_{A_2}	v_{A_1}	v_{A_2}
VI	1.0268	0.1073	576.2	60.21	0.001735	0.01661
V	0.9339	1621	524.1	90 97	1908	1099
III en IV	8581	2079	481.6	116.67	2076	08571
II	7557	2843	424.1	159 54	2358	06268

In the accompanying figure are given curves for the liquid and vapour densities and for the diameter constructed from the above values of d_k, d_1 and d_2, the liquid densities given by BALY and DONNAN and the critical temperature — 122°.44 C. of Comm. 115. The unconstrained manner in which the curves could be drawn through the points shewed that in the case of argon there was no necessity to expect any great deviation from the diameter law upon which the calculations were based.

Only the points of Series V (— 134°.72) do not appear to fit the curve so well, which is no doubt explained by an error of observation.

§ 4. *Representation of the observations by formulae.*

a. The purely empirical formula given by KEESOM [1]) is the most suitable one for this purpose; it may be written in the form

$$\left.\begin{aligned} \frac{d_1}{d_k} &= 1 + A\,(1-t) + B\,(1-t)^{\lambda} \\ \frac{d_2}{d_k} &= 1 + A\,(1-t) - B\,(1-t)^{\lambda} \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (1)$$

in which A, B, and λ are constants, and t represents reduced temperature.

By subtracting these equations the following simple relation is found for the observed magnitude $d_1 - d_2$:

$$d_1 - d_2 = 2d_k\,B\,(1-t)^{\lambda}.$$

With constants

$$\lambda = 0.3795 \text{ and } B = 1.999$$

determined by the observed values the following correspondence is obtained:

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[1]) W. H. KEESOM, Proc. April 1902, Comm. N⁰. 79.

Series	d_1-d_2 (O)	d_1-d_2 (C)	$O-C$ abs.	$O-C$ in %
VI	0.9195	0 9172	+ 0.0023	+ 0.2
V	7718	7874	— 0 0156	— 2.0
III and IV	6502	6493	+ 0 0019	+ 0 3
II	4714	4641	+ 0 0073	+ 1.5

If we calculate the constant A of (1) from the values of d_1 and d_2 deduced in § 3, the following correspondence is found for d_1 and d_2 as expressed by equation (1) with the value $A = 0.9758$.

Series	$d_1(O)$	d_1 (C)	$O-C$ abs.	$O-C$ in %	d_2 (O)	d_2 (C)	$O-C$ abs.	$O-C$ in %
VI	1.0268	1.0272	—0.0004	0.0	0.1073	0.1119	—0 0046	— 4.2
V	0.9339	0.9424	—0.0085	— 0.9	1621	1566	+0.0055	+ 3.4
III and IV	8581	8574	+0.0007	+ 0 1	2079	2094	0.0015	— 0.7
II	7557	7506	+0.0051	+ 0.7	2843	2875	—0.0032	— 1.1

The equations therefore give such results as might reasonably be expected from the accuracy of the observations, Slightly better results might of course be obtained by using least squares. The fact that the deviations of series V are on the whole greater than those of the other series may be explained by the suspicion already expressed that an error of observation has been made in that series.

b. GOLDHAMMER'S 1) formula, for $d_1 - d_2$ is

$d_1 - d_2 = m\, d_k (1 - t)^{1/3}$ 2).

With $m = 3.496$ the following correspondence is obtained:

Series	d_1-d_2 (O)	d_1-d_2 (C)	$O-C$ abs.	$O-C$ in %
VI	0.9195	0 8840	+ 0.0355	+ 3.8
V	7718	7731	— 0.0013	— 0.2
III and IV	6502	6526	— 0.0024	— 0.4
II	4714	4859	— 0.0145	— 3.1

The correspondence as might be expected is not nearly so good as that with KEESOM'S equation.

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1) D. A. GOLDHAMMER. Zs. f. phys. Chem. 71. 577. 1910.

2) This formula is almost identical with KEESOM'S, for KEESOM gives for pentane 0.3327 as the value of the index which I have called λ. To get as good an agreement as possible, however, I have made an independent calculation of this index for argon.

Physics. — "*Isotherms of monatomic gases and of their binary mixtures. VII. Isotherms of argon between + 20° C. and 150° C.*" By Prof. H. KAMERLINGH ONNES and C. A. CROMMELIN. Comm. N°. 118^b from the physical laboratory at Leiden.

(Communicated in the meeting of October 29, 1910).

§ 1. In the first publication[1]) of determinations of isotherms of gases at low temperatures made when these had already been a long time in progress mention was made of the desirability of an investigation of argon and helium; to these we may now add neon[2]). We were able to publish helium measurements as early as 1907[3]), but argon data were not accessible until a sufficient quantity of argon (about 25 L.) with not more than 0.1°/$_0$ impurity was obtained at a much later period (1909). The method of obtaining this has already been described[4]). This degree of purity is sufficient for isotherm determinations. Measurements of vapour pressures, of critical constants[4]) and also of coexisting liquid and vapour densities[5]) have already been made with the same gas as was used for the isotherms.

As was the case with hydrogen[6]) care was taken in the determination of the argon isotherms given below that the observed points should be appropriately distributed over each isotherm and that suitable temperatures for these should be selected. Still, the shape of the isotherms made it desirable that the points observed should not be so closely packed in normal positions as was the case with hydrogen.

Since all required densities cannot be obtained with one and the same piezometer reservoir, points for each isotherm must be divided into groups. The various groups of points which afterwards constitute a single isotherm were as far as possible observed at the same temperature by suitable adjustment of the cryostat pressure; corrections given by graphical evaluations of $\frac{d(pv_A)}{dt}$ were subsequently applied

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[1]) Proc. April 1901, Comm. No. 69.

[2]) Proc. June 1909, Comm. No. 112.

[3]) Proc. Dec. 1907, Febr. and March 1908, Comm. No. 102, a, b and c.

[4]) Proc. May 1910, Comm. No. 115, and C. A. CROMMELIN, Thesis for the doctorate, Leiden, 1910.

[5]) Proc. Dec. 1910 Comm. No. 118a.

[6]) Proc. March 1907. Comm, 97a, Dec. 1907, Comm. No. 99a, Dec. 1907, Comm. No. 100.

to reduce these to the same temperature. These corrections could not be made with the same degree of certainty as for hydrogen, for then the temperature differences were always less than 0°.2, while differences of fully 0°.4 were experienced in several instances in our present argon measurements.

That the individual coefficients [1]) for each isotherm may be calculated without adjustment from other isotherms, it is of special importance that points observed at temperatures which lie close together should be reduced to the same temperature.

There is yet another circumstance to cause the accuracy of the argon isotherms to be less than that reached in the hydrogen measurements. It has already been shewn [2]) that the desired degree of accuracy (from 1 to 0.5 per 1000) cannot be reached with reservoirs of content less than 5 cc. Hence the fact that quite a number of points have been got with a reservoir volume of 2.5 cc. can also account for the smaller degree of accuracy of many points. The following table gives for the various series rough values of the volumes in cc. of the large reservoir in the compression chamber and of the small reservoir that is kept at low temperature.

Series.	Large reservoir.	Small reservoir.
I—XII	600	2.5
XIII—XVIII	2000	5
XIX—XXI	600	2.5
XXII—XXIII	600	5
XXIV—XXXV	600	15
XXXVI—XXXVIII	600	2.5

§ 2. The argon used was made according to the methods indicated in § 1—3 Part I of Comm. 115. For the sake of completeness we now publish some further diagrams of the apparatus used.

Fig. 1 [3]) shews the circulating apparatus following that used by FISCHER and RINGE [4]).

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[1]) Proc. June 1901, Comm. No. 71.

[2]) Proc. April 1901 Comm. No. 69 § 6, and Proc. March 1903, Comm. No. 84 § 19.

[3]) Proc. May 1910, Med. 115, Part I § 1*b*.

[4]) F. FISCHER and O. RINGE. Ber. d.d. chem. Ges. 41. 2017. 1908.

A, a dry gas meter, (air inlet).

B, two potash drying towers.

C, three iron tubes[1] containing a mixture of 90% calcium carbide and 10% calcium chloride, heated in a coke furnace so as to absorb oxygen and nitrogen.

D, a porcelain tube containing copper oxide, and heated in a chemical combustion furnace so as to get rid of hydrocarbons (especially acetylene).

E, two drying tubes containing potash and phosphorus pentoxide.

F, a mercury jet circulating pump (more detailed in Fig. 2).

G, Töpler pump for drawing off the gas that has been treated and an oil gasometer for storing it in.

During the working cycle the valves C_1 and C_2 are closed; the gas travels the path indicated by arrows.

Fig. 2.[2] Apparatus for a working cycle over Hempel mixture.

A, iron tube containing Hempel mixture, and heated in a chemical combustion furnace for absorption of nitrogen.

B, a hard glass tube of copper oxide heated in a small furnace to absorb traces of hydrocarbons that come from the mixture.

C, two drying towers filled with potash and phosphorus pentoxide.

D, circulating pump: a Prytz-pump D_1 worked by an electric motor D_2 raises the mercury. The mercury does not pass through any taps, and the apparatus can be evacuated without allowing any air to force its way in through the pump. The pump can be worked for all pressures in the apparatus less than 1 atm. If the tube of the Prytzpump breaks the gas in the apparatus can neither escape nor be contaminated.

E, side tubes for removing and supplying gas.

F, manometer.

G, two vessels each of about 5 L. content, to increase the capacity of the apparatus.

H, phosphorus pentoxide drying tube.

I, a side tube to allow of the removal of the gases developed when the Hempel mixture is heated at the beginning.

J, side tube for the removal of the purified gas, which is then stored in a high pressure cylinder as shown in Fig. 3.

Fig. 3.[3] Apparatus for the separation of argon and neon by fractional distillation.

A, High pressure cylinder containing argon still contaminated with neon.

B, manometer.

C, reservoir surrounded by liquid oxygen boiling under strongly reduced pressure; in this the argon freezes. A mercury suction pump *E* brings the neon along *D* to the bulb *F*. A Töpler pump then removes the argon along *G*. *H* is the pressure side of this pump, from which the argon at an over pressure of about 1 atm. is passed into the chamber *I*, immersed in liquid air boiling under reduced pressure. When that chamber is filled with solid argon, it is warmed, and the gas blows off to the pure gas storage cylinder *J*.

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[1] These tubes, have already served for the preparation of helium, cf. Proc. May-June 1908, Comm. N°. 108.

[2] Proc. May 1910. Comm. N°. 115, Part. I § 1*c*.

[3] Proc. May 1910. Comm. N°. 115, Part. I. § 3,

§ 3. For description of the *apparatus* used for determinations of the normal volume and of the individual isotherms we may refer to earlier publications [1]. In one respect we introduced an improvement for we took our readings through a telescope with a micrometer eye piece; in this way they could be made at twice the rate possible when using the nonius of the cathetometer. Pressure and temperature readings were made in exactly the same manner as before in determinations of vapour pressures etc., [2] and the remarks made in the communication of those results apply equally well here. Measurements of pressures below 20 atm. were made with the standard open manometer. [3]

We gratefully acknowledge our indebtedness to Miss G. L. LORENTZ and Mr. W. J. DE HAAS for their measurements and calculation of the temperatures, and also to Dr. C. DORSMAN Jr., and Mr. G. HOLST for their measurements with the open manometer.

§ 4. As regards the calculations themselves we may also refer to earlier communications [4] for there is not much fresh to be said about them. First, isotherms for + 20° C. and 0° C. were calculated using the expansion coefficients for oxygen taken from an earlier paper [5]; the critical constants for argon and oxygen differ but slightly from each other. Then the coefficients of the empirical equation of state [6] A_A and B_A were calculated to a first approximation, and using the critical constants [7] a value for C_A was got from the set of reduced coefficients VII. 1 [8]. From the equation to which the operations led the expansion coefficients for various densities were calculated, and with these values the calculation of the isotherms was repeated. From these new isotherms to a second approximation, the coefficients were recalculated to a second approximation. For our present purpose a third approximation was found to be unnecessary.

The expansion coefficients at low temperatures which were necessary for the much smaller corrections for that portion of the glass capillary inside the cryostat were at first deduced from AMAGAT's [9]

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[1] Proc. April 1901, Comm. N⁰. 69, Proc. April 1902. Comm. N⁰. 78. Proc. Sept. 1906, Comm. N⁰. 94*f*, Proc. March 1907, Comm. N⁰. 97*a*.

[2] Proc. May 1910, Comm. N⁰. 115.

[3] Proc. Nov. 1898. Comm. N⁰. 44.

[4] Proc. April 1902, Comm. N⁰. 78, Proc. March 1907, Comm. N⁰. 97*a*.

[5] Proc. April 1902, Comm. N⁰. 78.

[6] Proc. June 1901, Comm. N⁰. 71.

[7] Proc. May 1910, Comm. N⁰. 115.

[8] Suppl. N⁰. 19. (May 1908) p. 18.

[9] E. H. AMAGAT. Ann. d. Chim. et d. phys (6). 29, June and Aug. 1893.

oxygen isotherms with the aid of the law of corresponding states. Subsequently, when we could avail ourselves of a portion of our experimental data, the expansion coefficients or rather the densities which are in this case easier to manipulate were graphically determined. The degree of accuracy afforded by this method was found to be quite sufficient for our purpose. The second approximations were found to be sufficient for all the isotherms.

In the calculations we have made no use of the RAMSAY and TRAVERS [1]) isotherm at + 11°.2 C., for their observations shewed such marked deviations from ours that we could place no reliance upon them.

§ 5. The *results* are contained in the following tables. In the first column is given the date, in the second the series, and in the third the number of the observation; in the fourth is given the temperature in Kelvin degrees [2]) — 273°.09; the fifth and sixth contain the pressure in atmospheres (p) and the density in terms of the normal density respectively, the results gives the product of p into the volume expressed in terms of the normal volume pv_A and finally the eighth contains the values of v_A.

Such observations as were for any reason deemed less accurate than the others are placed between square brackets.

Observations marked by an asterisk were made by way of control after the measurements proper were completed because uncertain indications of one of the metal manometers made us for a moment suspect that something had happened to the pressure measurement. The table of deviations given in a subsequent section shows that this fear was baseless.

§ 6 A general survey of the region which the present isotherms in connection with earlier papers [3]) enable us to regard as known is given by the accompanying pv_A diagram for all observations [4]). Observed points are represented by small circles. For data for the boundary curve we may refer to the other papers just mentioned. Points calculated from the liquid and vapour densities are given by squares, and points extrapolated from the isotherms are given by triangles [5]).

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[1]) W. RAMSAY and M. W. TRAVERS. Phil. Trans. (A) 197, 47, 1901.

[2]) Proc. Dec. 1907. Comm. N°. 101b.

[3]) Proc. May 1910. Comm. 115, Proc. Dec. 1910, Comm. N°. 118*a*.

[4]) Fig. 5.

[5]) In order to make the diagram not uselessly long, the volumes above 0.040 are omitted. The isotherms of + 20°.39 C., 0°.00 C. and – 57°.72 C. therefore ought to have been drawn until the line $v_A = 0.040$.

Isotherms of argon. TABLE I*a*.

Data.	Series.	No.	θ	p	d_A	pv_A	v_A
May 11, 1910	XXXV	1	+20°.39	21.783	20.499	1.0627	0.048783
» »	XXXV	2		27.320	25.759	666	38821
» »	XXXV	3		34.487	32.590	582	30684
July 2, »	XXXVIII	1		*37.248	35.330	543	28305
Dec. 23, 1909	X	1		37.673	35.759	535	27965
» »	X	2		49.604	47.319	483	21134
July 2, 1910	XXXVIII	2		*61.697	59.134	434	16911
Dec. 23, 1909	X	3		61.741	59.250	420	16878
Dec. 23, 1909	IX	1	+18°.39	37.264	35.401	1.0526	0.028248
» »	IX	2		49.586	47.355	471	21117
» »	IX	3		62.489	60.060	465	16650
May 11, 1910	XXXIV	1	0°.00	20.576	20.877	0.98560	0.047900
» »	XXXIV	2		26.070	26.581	98077	37621
» »	XXXIV	3		31.572	32.302	97740	30958
Dec. 22, 1909	VIII	1		36.743	37.782	97250	26468
» »	VIII	2		49.871	51.840	96201	19290
» »	VIII	3		62.230	65.325	95261	15308
May 10, 1910	XXXII	1	−57°.72	17.872	23.509	0.76023	0.042537
» »	XXXII	2		[21.488	28.577	75200	34996]
» »	XXXII	3		25.228	33.793	74654	29592
Dec. 20, 1909	VI	1		35.127	48.116	73004	20783
» »	VI	2		46.209	64.948	71148	15397
» »	VI	3		62.079	90.695	68448	11026
May 10, 1910	XXXIII	1	−87°.05	16.178	25.152	0.64320	0.039758
» »	XXXIII	2		21.651	34.467	62816	29013
Dec. 21, 1909	VII	1		33.296	55.822	59646	17914
» »	VII	2		41.094	71.444	57519	13997
» »	VII	3		51.533	94.625	54460	10568
» »	VII	4		61.830	119.84	51594	0.0083446

Isotherms of argon. **TABLE Ib.**

Data.	Series.	No.	θ	p	d_A	pv_A	v_A
May 6, 1910	XXXI	1	—102°.51	14.864	25.571	0,58130	0,039107
»	XXXI	2		19.790	35.077	56420	28509
Apr. 6,	XXII	1		[26.143	47.893	54587	20880]
»	XXII	2		[28.840	53.752	53654	18604]
Dec.14, 1909	I	1		32.394	62.240	52047	16067
Apr. 6, 1910	XXII	3		[35.784	69.954	51153	14295]
Dec.14, 1909	I	2		40.976	84.002	48780	11904
»	I	3		45.088	95.802	47063	10438
	I	4		51.398	115.88	44354	0.0086296
	I	5		56.882	135.65	41935	73722
»	I	6		62.239	158.01	39388	63286
May 6, 1910	XXX	1	—109°.88	14.443	26.242	0.55039	0.038107
»	XXX	2		18.653	34.807	53589	28730
Dec.18, 1909	V	1		31.515	65.142	48379	15351
July 1, 1910	XXXVII	1		*31.929	66.530	47993	15031
Dec.18, 1909	V	2		39.166	87.176	44927	11471
» »	V	3		43.718	102.76	42544	0.0097315
» »	V	4		49.515	125.56	39435	79642
»	V	5		54.250	148.32	36577	67424
July 1, 1910	XXXVII	2		*54.859	152.79	35929	65451
Dec.18, 1909	V	6		59.616	180.84	32966	55298
Dec.17, 1909	IV	1	—113°.80	31.001	67.078	0.46216	0.014908
	IV	2		38.005	88.889	42756	11250
» »	IV	3		42.682	106.68	40010	0.0093741
»	IV	4		47.655	129.17	36894	77410
March 4, 1910	XV	1		51.752	152.71	32889	65483
Dec.17, 1909	IV	5		52.188	155.40	33583	64350
March 4, 1910	XV	2		55.763	182.13	30617	54905
Dec.17, 1909	IV	6		55.991	184.82	30295	54107
March 4, 1910	XV	3		58.898	212.99	27653	46950

Isotherms of argon. TABLE I*c*.

Data.	Series.	No.	θ	p	d_A	pv_A	v_A
Dec.15, 1909	II	1	—115°.86	31.323	69.947	0.44781	0.014296
» »	II	2		37.788	91.308	41385	10952
» »	II	3		41.908	108.02	38796	0.0092574
» »	II	4		46.648	131.51	35469	76037
» »	II	5		50.324	155.12	32442	64464
March 2, 1910	XIV	1		53.204	179.94	29568	55575
Dec.15, 1909	II	6		[54.865	183.35	29923	54539]
March 2, 1910	XIV	2		57.493	235.47	24416	42468
» »	XIV	3		61.626	319.52	19287	31297
May 4, 1910	XXVIII	1	—116°.62	13.863	26.480	0.52353	0.037765
» »	XXVIII	2		17.697	34.939	50650	28621
Dec.16, 1909	III	1		30.681	68.630	44705	14571
» »	III	2		37.250	90.563	41131	11042
» »	III	3		41.943	110.19	38063	0.0090749
» »	III	4		46.496	133.69	34779	74800
» »	III	5		50.259	159.71	31468	62612
March 2, 1910	XIII	1		50.447	161.75	31189	61824
Dec.16, 1909	III	6		[53.059	186.15	28503	53719]
March 2, 1910	XIII	2		54.922	210.02	26151	47615
» »	XIII	3		[57.617	260.61	22108	38371]
» »	XIII	4		60.669	331.29	18313	30185
May 6, 1910	XXIX	1	—119°.20	13.766	26.871	0.51230	0.037215
» »	XXIX	2		17.378	34.965	49700	28600
Jan. 7, »	XI	1		[30.376	70.314	43200	14222]
March 16, »	XIX	1		30.303	70.481	42994	14188
July 1, »	XXXVI	1		*30.365	70.580	43021	14168
March 16, »	XIX	2		34.052	83.257	40900	12011
Jan. 7, »	XI	2		37.641	96.834	38872	10327
March 16, »	XIX	3		37.923	98.863	38359	10115
» »	XIX	4		43.006	124.97	34414	0.0080022
Jan. 7, »	XI	3		[46.082	143.71	32065	69583]
March 16, »	XIX	5		47.272	156.36	30233	63955
March 4, »	XVI	1		[49.294	172.25	28617	58054]
» »	XVI	2		51.679	222.69	23207	44906
» »	XVI	3		53.044	275.02	19287	36361
» »	XVI	4		54.244	336.89	16101	29683

Isotherms of argon. TABLE I*d*.

Data.	Series.	No.	θ	p	d_A	pv_A	v_A
March 16, 1910	XX	1	−120°.24	30.809	72.627	0.42421	0.013769
» »	XX	2		33.776	82.816	40784	12075
» »	XX	3		37.836	99.246	38124	10076
» »	XX	4		41.668	118.51	35160	0.0084380
» »	XX	5		44.510	136.31	32654	73363
March 5, »	XVII	1		47.705	165.79	28774	60317
» »	XVII	2		50.351	206.57	24375	48410
» »	XVII	3		52.253	280.25	18645	35682
» »	XVII	4		53.191	338.95	15693	29503
May 4, 1910	XXVII	1	−121°.21	13.754	27.326	0.50333	0.036595
» »	XXVII	2		17.225	35.283	48818	28342
March 17, »	XXI	1		30.122	71.459	42153	13994
» »	XXI	2		34.070	85.580	39811	11685
» »	XXI	3		37.465	100.33	37343	0.0099674
» »	XXI	4		[41.932	123.85	33856	80741]
» »	XXI	5		45.282	148.95	30402	67139
March 5, »	XVIII	1		47.094	170.05	27693	58805
» »	XVIII	2		49.865	234.13	21298	42711
» »	XVIII	3		50.885	333.75	15247	29963
Apr. 28, 1910	XXIV	1	−130°.38	12.773	27.394	0.46625	0.036504
» »	XXIV	2		[14.384	31.583	45430	31663]
» »	XXIV	3		15.664	34.726	45108	28797
Apr. 6, »	XXIII	1		22.861	55.807	40964	17919
» »	XXIII	2		25.519	65.125	39185	15355
Jan. 7, »	XII	1		28.878	77.821	37108	12850
» »	XII	2		[32.993	101.71	32438	0.0098318]
Apr. 30, 1910	XXV	1	−139°.62	11.986	28.122	0.42620	0.035559
» »	XXV	2		14.586	35.573	41003	28111
Apr. 30, 1910	XXVI	1	−149°.60	11.450	29.183	0.38205	0.034266
» »	XXVI	2		12.788	34.646	36910	28863

Finally, a diagram of the $\frac{pv_A}{T}$, d_A isotherms is added to this paper[1]).

§ 7. *Individual virial coefficients.*[2])

An attempt was made to represent the isotherms by the empirical equation of state

$$pv_A = A_A + \frac{B_A}{v_A} + \frac{C_A}{v^2_A} + \frac{D_A}{v^4_A} + \frac{E_A}{v^6_A} + \frac{F_A}{v^8_A},$$

and to evaluate the individual virial coefficients.

Seeing that we could not avail ourselves of measurements at such small densities as was the case with hydrogen and hence could not calculate values of A_A for each individual isotherm from the observations, the calculation was made by means of the equation

$$A_{A_T} = A_{A_0}(1 + 0.0036618\,\theta)$$

A_{A_0} was first calculated as accurately as possible from

$$A_{A_0} = 1 - B_{A_0} - C_{A_0}$$

since for $p = 1$, $v_{A_0} = 1$ and D_{A_0} etc. may be made $= 0$) and

Individual virialcoefficients of argon. TABLE II.

t	A_A	$10^3.B_A$	$10^6.C_A$	$10^{12}D_A$	$10^{18}E_A$	$10^{24}F_A$
+20°.39	+1.07545	−0.60271	+0.66360	*+4.32836*		
0°.00	**+1.00074**	−0.73969	+0.00487	*+3.09635*		
−57°.72	+0.78922	−1.30460	+1.64016	*−0.67139*		
−87°.05	+0.68174	−1.63902	+2.12711	*−2.83014*	*+10.5566*	
−102°.51	+0.62511	−1.81649	+2.28125	*−4.10121*	*+10.4013*	
−109°.88	+0.59810	−1.92881	+2.57060	*−4.76310*	*+10.3251*	
−113°.80	+0.58372	−1.97263	+2.36239	+2.40001	*+10.2947*	
−115°.86	+0.57617	−2.03892	+2.74407	−2.45810	*+10.2837*	*−2.35600*
−116°.62	+0.57340	−2.02273	+2.56235	−1.20499	*+10.2806*	*−2.31432*
−119°.20	+0.56393	−2.04406	+2.31445	+0.65126	*+10.2759*	*−2.17669*
−120°.24	+0.56012	−2.05472	+2.50248	−0.67211	*+10.2764*	*−2.12239*
−121°.21	+0.55658	−2.05084	+2.37741	+0.13359	*+10.2783*	*−2.07246*

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[1]) Fig. 4.

[2]) Proc. June 1901. Comm. N°. 71.

Deviations of pv_A in percents of $pv_A(R)$ TABLE III.

+20°.39		0°.00		−57°.72		−87°.05		−102°.51		−109°.88	
d_A	$W-R$ in %	d_A	$W-R$ in %	d_A	$W-R$ in %	d_A	$W-R$ in %	d_A	$W-R$ in %	d_A	$W-R$ in %
20.499	−0.07	20.877	+0.03	23.509	+0.10	25.152	+0.21	25.571	+0.20	26.242	+0.21
25.759	+0.02	26.581	−0.03	[28.575	−0.17]	34.467	+0.06	35.077	0.00	34.807	+0.34
32.590	+0.16	32.302	+0.06	33.793	−0.06	55.822	−0.06	[47.893	+0.47]	65.142	+0.11
*35.330	−0.07	37.782	−0.03	48.116	−0.03	71.444	−0.05	[53.752	+0.47]	*66.530	−0.24
35.759	−0.12	51.840	−0.04	64.948	+0.01	94.625	−0.16	*62.240	+0.08	87.176	+0.01
47.319	−0.01	65.325	+0.02	90.695	+0.01	119.84	+0.12	[69.954	+0.48]	102.76	−0.25
59.134	+0.12							84.002	−0.13	125.56	−0.24
*59.250	+0.01							95.802	−0.22	148.32	−0.17
								115.88	−0.22	*152.79	−0.46
								135.65	0.00	180.84	+0.31
								158.01	+0.31		

−113°.80		−115°.86		−116°.62		−119°.20		−120°.24		−121°.21	
d_A	$W-R$ in %	d_A	$W-R$ in %	d_A	$W-R$ in %	d_A	$W-R$ in %	d_A	$W-R$ in %	d_A	$W-R$ in %
67.078	+0.02	69.947	−0.20	26.480	+0.36	26.871	+0.32	72.627	+0.03	27.326	+0.20
88.889	+0.09	91.308	+0.27	34.939	+0.13	34.965	+0.34	82.816	+0.18	35.283	+0.21
106.68	−0.09	108.02	+0.07	68.630	+0.10	[70.314	+0.08	99.246	+0.12	71.459	−0.15
129.17	−0.03	131.51	−0.06	90.563	+0.03	70.481	−0.33	118.51	−0.02	85.580	−0.10
152.71	−0.03	155.12	−0.12	110.19	−0.22	*70.580	−0.23	136.31	+0.05	100.33	−0.06
155.40	+0.02	179.94	−0.19	133.69	−0.19	83.257	−0.23	165.79	−0.07	[123.85	−0.10]
182.13	+0.11	[183.35	+2.24]	159.71	−0.13	96.834	+0.24	206.57	+0.72	148.95	0.00
184.82	−0.03	235.47	+0.35	161.75	−0.23	98.863	−0.25	280.25	(+2.71)	170.05	0.00
212.99	+0.04	319.52	−0.09	[186.15	+0.17]	124.97	−0.20	338.95	−0.00	234.13	(+1.95)
				210.02	(+0.52)	[143.71	+0.72]			333.75	0.00
				[260.61	+1.44]	156.36	+0.26				
				331.29	−0.05	[172.25	+1.68]				
						222.69	(+2.47)				
						275.02	(+4.12)				
						336.89	−0.12				

$$pv_{A_0} = 1 - B_{A_0} - C_{A_0} \; ; \quad \frac{B_{A_0}}{v_{A_0}} \; , \quad \frac{C_{A_0}}{v^2_{A_0}}$$

And seeing on the other hand that the densities attained are not sufficiently great to allow of the calculation of the last coefficients, values of E_A and F_A and sometimes too of D_A (insofar as they had to be allowed for) were obtained by combining the critical constants published a short time ago with the set of reduced virial coefficients VII. 1. Solutions for the other coefficients were then obtained for each isotherm from a number of suitable chosen points, and were tested with the observed results. Finally, correspondence was made as satisfactory as possible either by least squares or by the method of E. F. VAN DE SANDE BAKHUYZEN [1]).

In this way the individual coefficients for each isotherm given in table II were obtained. Numbers borrowed from the reduced coefficients VII. 1., are printed in italics.

With these coefficients values of pv_A were calculated; table III gives percentage deviations of calculated results from observed ones. In this table [ ] and * have the same significance as before. Deviations placed between ( ) are so treated because the observations to which they belong were not used in the adjustment of coefficients; this was done from consideration of the difficulty of obtaining agreement with a formula of whose constants only three are derived from observations in that neighbourhood.

Chemistry. — *"On the reaction products of potassium isocyanate and diaminoacetone hydrochloride. Amino- and ureopropylene-ureïne."* By Prof. A. P. N. FRANCHIMONT and Dr. J. V. DUBSKY.

(Communicated in the meeting of November 26, 1910).

More than three years ago (February 23 1907) I called attention to the importance which the knowledge of acetoneureïne would have in answering the question as to the action of nitric acid on heterocyclic compounds consisting of two CO-, two NH- and two CH_2 groups. Of the eleven theoretically possible isomers, there are two which are urea derivatives, namely hydro-uracil and acetoneureïne. The first has been investigated as to its behaviour with nitric acid by myself and FRIEDMANN, the second has not been obtained as yet.

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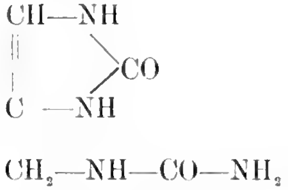
[1]) Proc. July 1906, Comm. No. 95a.

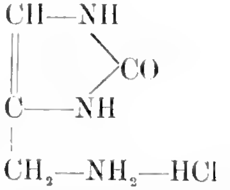
Attempts with Dr. **Friedmann** to prepare it from diaminoacetone hydrochloride, although not having led to the desired result, still showed that a substance obtained by **Rügheimer** in 1892 by the action of chloroformic ester on diaminoacetone and which he supposed to be acetone-ureïne, although no analysis of it was made, can have been nothing else than acetonediurethane.

We have now continued these investigations and have succeeded in elucidating the reaction with potassium isocyanate, although this also has not led to the desired result. **Rügheimer** had pretended in 1892 that a *diureo-acetone* would form which, however, was so unstable that he could not isolate the same and that it was converted at the ordinary temperature with loss of ammonia into a substance which he called *acetonylbiuret* [1]), in which he determined the carbon and hydrogen but not the nitrogen; at least he does not give the percentage. Had he done so, he would probably have found that it possesses quite a different composition, not $C_5H_7O_3N_3$ as he states, but $C_5H_8O_2N_4$ which we have found for the compound formed by the action of two mols. of potassium isocyanate on one mol. of diaminoacetone hydrochloride in aqueous solution. By the action of one mol. of isocyanate, a chlorinated substance, having the composition $C_4H_8ON_3Cl$, is formed, which on being treated with a second mol. of isocyanate, yields the first product. In consequence of the analogy with a number of other well-known reactions we take it for granted that as soon as a ureo-group has formed, this acts with its NH_2-group on the CO of the acetone residue, when a cyclic compound is generated with formation of water.

The following formulae will have to be assigned to the two compounds obtained; although other ones might be proposed, they are amply confirmed by the derivatives obtained.



Ureopropyleneureïne.



Aminopropyleneureïne hydrochloride.

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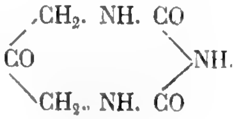
[1]) To which he assigned the formula 

The name chosen is in agreement with the one formerly used by myself and others.

Aminopropyleneureïne hydrochloride which, as already stated, is obtained from one mol. of potassium isocyanate and one mol. of diaminoacetone hydrochloride in aqueous solution crystallises in beautiful small needles which are very soluble in water. Up to the present we have not isolated from it the free aminopropyleneureïne but have prepared a few of its compounds with other acids and also a number of other derivatives.

With the calculated amount of silver nitrate in aqueous solution, in the cold, the *nitric compound* was formed which may be precipitated by addition of alcohol; this also forms beautiful small needles.

The *acid sulphuric compound* was obtained by treating the hydrochloride, in the cold, with sulphuric acid and removing the hydrogen chloride in a vacuum and freeing the residue from the excess of acid by means of alcohol and ether. The *neutral sulphuric compound* was prepared from lead isocyanate and diaminoacetone sulphate and was purified by precipitation with alcohol.

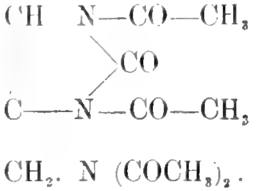
The four compounds, which have all been analysed, form delicate colourless small needles, which have no real melting point, but are decomposed on heating at various temperatures.

When boiled with acetic anhydride and sodium acetate for five minutes the hydrochloride yielded a *triacetyl derivative*, which if recrystallised from benzene forms small delicate needles melting at 141°.

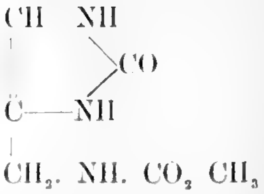
On further boiling, a *tetracetyl derivative* was obtained, which crystallised from alcohol containing a little acetic acid in small, beautiful, square plates melting at 163°—164°.

The composition of these acetyl derivatives is derived from the results of the elementary analysis, because acetyl determinations, even those according to PERKIN, did not yield good results.

The composition of the tetracetyl compound in which, presumably, two acetyl groups have entered into the NH_2 group, and two into the NH groups of the ureïne, and which then has this formula:



is a peculiar one.



With methyl chloro-formate and sodium carbonate in aquous solution, aminopropylene ureïne hydrochloride yields a *carboxymethyl derivative* (a urethane), which, when recrystallised from alcohol, forms glittering leaflets, which melt at 238° with decomposition. From this was prepared, by five minutes boiling with acetic anhydride, a *monoacetyl derivative* which crystallises from ethyl acetate in splendid needles, melts at 215°, and is decomposed when heated a trifle above that temperature.

A *diacetyl derivative* was obtained by boiling for an hour with acetic anhydride; this yields also splendid needles and melts at 125°—126°.

The two acetyl groups will, therefore, most probably be attached to the nitrogen atoms of the ureïne. and no acetyl has arrived at the urethane function.

The corresponding *carboxethyl derivative* was also prepared; this crystallises from boiling alcohol in small very glittering crystals melting at 208°. In the same manner as in the case of carboxymethyl derivative, a *monoacetyl compound* was obtained therefrom, which crystallises from acetic acid in beautiful, silky needles, melting at 218°—219°, and also a *diacetyl compound*, melting at 101°—102°.

Ureopropyleneureïne was obtained, not only from diaminoacetone hydrochloride with two mols. of potassium isocyanate in aqueous solution, but also from aminopropyleneureïne hydrochloride with one mol. of isocyanate. When crystallised from boiling water (it is but little soluble in cold water), it forms snow-white leaflets, which have no melting point, but are decomposed with change of colour at a little over 220°. It is soluble without decomposition in boiling acetic acid, and in this solvent the molecular weight was determined.

In aqueous solutions it gives no precipitates with silver nitrate and mercuric chloride unless ammonia is added, but it is precipitated by mercuric nitrate and therefore, behaves in this respect like urea.

On being boiled with acetic anhydride the bulk remained at first unaltered and it took ten hours to effect the change. The tetracetyl compound of aminopropyleneureïne was thus obtained and recognised by its form and melting point: the urea residue has, therefore, been broken up.

Finally, it should be mentioned that diacetylaminoacetone is also converted on prolonged boiling with an excess of acetic anhydride into tetracetyldiaminoacetone. When crystallised from boiling benzene, or from alcohol, it forms long, very lustrous needles which cake at 98° and melt at 103°.

Mathematics. — *Double points of a c_6 of genus 0 or 1.* By Dr. W. VAN DER WOUDE. (Communicated by Prof. SCHOUTE.)

(Communicated in the meeting of November 26, 1910).

§ 1. A curve of order n is in general determined by $\frac{1}{2}n(n+3)$ single conditions. So a curve of order five is determined by 20 points, or — a node counting for 3 single data — by 6 double points and 2 single points. However, it is not possible to take arbitrarily the double points of a rational curve of higher order than the fifth; for the number of double points of this curve amounts to $\frac{1}{2}(n-1)(n-2)$ and for $n > 5$ three times this amount is larger than $\frac{1}{2}n(n+3)$. Between the double points of a curve of order n whose number of double points is greater than $\frac{1}{6}n(n+3)$ one or more relations must exist. "So far no attempt seems to have been made to express those relations geometrically"; [1]) in the following paragraphs I intend to do this with reference to the curve of order six.

§ 2. A curve of order six is determined by 27 single data, hence by 27 points. It can possess at most 10 double points; according to the preceding 9 of these can be taken arbitrarily and really a curve of order six is determined by 9 double points taken arbitrarily; this is however degenerated into a cubic curve to be counted double through those 9 points.

If therefore a (non-degenerated) curve of order six has 9 double points, there must be a relation between these already; only 8 can be taken arbitrarily. In future we shall understand by $D_1, D_2, \ldots, D_8$ points taken arbitrarily; the locus of the point forming together with these a system of 9 double points of a curve of order six not degenerating into a cubic curve to be counted double we shall for the present represent by j_n, whilst by c_n an arbitrary curve of order n is meant.

§ 3. If D_9 is a point of j_n there exists a (non-degenerated) curve of order six possessing a double point in each of the points $D_1, D_2, \ldots D_9$; furthermore we can lay through these 9 points a cubic curve. If these

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[1]) SALMON FIEDLER, Höhere ebene Kurven, p. 42.

two curves are represented respectively by the equations $w_6 = 0$ and $u_3 = 0$, then by $w_6 + \lambda u^2_3 = 0$ a pencil of curves of order six is determined, each of which possesses in each of the base points of the pencil a double point. Hence

If D_1, $D_2 \ldots D_9$ are double points of a curve of order six not degenerating into a cubic curve to be counted double, these points are the base points of a pencil of curves of order six with nine common double points.

For shortness'sake we shall in future call such a pencil a c_6 pencil with 9 double points; of course through each point passes *one* curve of this pencil.

§ 4. Out of the c_3 pencil determined by the base points D_1, $D_2 \ldots D_8$ we choose one u_3; we furthermore introduce a variable c_6, possessing double points in D_1, $D_2 \ldots D_8$, but being for the rest undetermined. These two curves intersect each other in 2 more points; the line connecting these two points intersects u_3 in another point T. This last point is according to the *Residual Theory* of SYLVESTER a fixed point, i. e. independent of the c_6 chosen by us. Point T is easy to determine; it is evident that if we take for c_6 a c_3 counting double, T is the tangential point of B_9, the ninth base point of the c_3 pencil through D_1, $D_2 \ldots D_8$.

If of a pencil c_6 the double points D_1, $D_2 \ldots D_8$ and a point P are determined, then according to the preceding another point P' of c_6 is determined; if namely we lay through D_1, $D_2 \ldots D_8$ and P a cubic u_3 and if we determine on it the tangential point T of B_9, then the third point of intersection of TP with u_3 is the point P' under discussion. Farthermore it is evident from this that only these points of u_3 having T as tangential point *can* be the ninth double points of a c_6, which has already double points in D_1, $D_2 \ldots D_8$. If however we impose the condition that this c_6 may not have degenerated into a c_3 counting double, then one of these points, viz. B_9 does not count; for, there is not a single non-degenerated c_6 which has double points in D_1, $D_2 \ldots D_8$ and B_9. For then we should be able to bring a c_3 through these points and a point chosen arbitrarily on the curve c_6 and the curves c_3 and c_6 would have nineteen points in common. If however J, J', and J'' are the other points of u_3 having T as tangential point, then each c_6, having double points in D_1, $D_2 \ldots D_8$ and passing through one of these points, will have there two points in common with u_3.

§ 5. We can determine a c_6 pencil by the double points D_1, $D_2 \ldots D_8$

and 2 points P and Q chosen arbitrarily; the two other base points of the pencil P' and Q' are then by this completely determined. From the preceding is evident, how we can determine those two last points and also, that *one* of these points e. g. P' is independent of Q and the other Q' of P.

We now again understand by u_3 an arbitrary cubic through $D_1, D_2 \ldots D_8$, whilst also J, J' and J'' have the same meaning as in § 4. We then further regard the c_6 pencil (β), having $D_1, D_2 \ldots D_8$ as double points and moreover J and an arbitrary point Q as single base points. An arbitrary curve out of (β) will touch u_3 in J whilst the last base point of (β) lies on the c_3 through $D_1, D_2 \ldots D_8$ and Q and is to be determined in the way indicated above; the line touching in J the u_3 as well as an arbitrary curve out of (β) we shall call j. If we then draw through J an arbitrary line l and if A is a point moving along l, then always through A passes *one* curve a_6 out of the pencil (β); if we allow A to coincide with J then the lines j and l will both have in J two points in common with a_6. From this ensues that J is now a double point of a_6 and lies therfore on the curve which we have indicated by j_n.

If inversely it is given that J is a point of j_n and if we bring a c_3 through $D_1, D_2 \ldots D_8$ and J, then J must possess the same tangential point on c_3 as B_9. We have then proved:

If we generate a c_6 pencil with double points in the points D_1, $D_2 \ldots D_8$ chosen arbitrarily and single base points in a point J of the curve j_n and in a point Q chosen arbitrarily, then the curves of this pencil have in J a common tangent. In this pencil is included a curve, having in J a ninth double point.

§ 6. We have seen, that on an arbitrary curve u_3 out of the c_3 pencil having $D_1, D_2 \ldots D_8$ and B_9 as base points lie three points of j_n; these points have on u_3 the same tangential point T as B_9. We now regard first the locus of T when u_3 describes the c_3 pencil which we shall now call (β'). Each line l through B_9 determines *one* curve out of (β'), touching it; so l intersects the indicated locus besides in B_9 in *one* point. Farthermore this locus has in B_9 a triple point, three curves out of (β') possessing in B_9 a point of inflexion. The point T describes therefore a quartic curve t_4 possessing in B_9 a triple point; the points $D_1, D_2 \ldots D_8$ lie also on t_4, as each of the lines B_9D is touched by *one* curve.

Let T' be the tangential point of D_1 on u_3, then if again u_3 describes the pencil (β'), T' describes a quartic curve t'_4; t_4 and t'_4 have besides the base points of (β') three more points in common, which points to the fact that three times one and the same point is at the same time tangential point of B_9 and D_1. If, however, B_9 and D_1 have on a curve out of (β') the same tangential point, then D_1 will lie on the curve j_n. This last will be cut by u_3 in each of the points D_1, $D_2 \ldots D_8$ three times and once in three other points; so it is of order nine.

If D_1, $D_2 \ldots D_8$ *are points chosen arbitrarily, then the locus of the point which can be the ninth double point of a curve of order six already possessing double points in* $D_1, D_2 \ldots D_8$ *is a curve* j_n *of order nine with triple points in* D_1, $D_2 \ldots D_8$.

Moreover we have found the following generation of j_n:

If we determine on a curve u_3 *out of the* c_3*-pencil* (β') *with the base points* $D_1, D_2 \ldots, D_8$ *the points having the same tangential points, as the ninth base point* B_9, *then if* u_3 *describes the pencil* (β') *these points will describe the curve* j_n.

§ 7. We shall now show analytically that the curve j_n is of order nine and possesses triple points in $D_1, D_2, \ldots D_8$.

To this end we regard the net of curves $\mathbf{r} \equiv w_6 + \lambda u^2_3 + \mu v^2_3 = 0$, where $w_6 = 0$ represents a curve of order six with double points in $D_1, D_2 \ldots D_8$, whilst $u_3 = 0$ and $v_3 = 0$ are the equations of two cubic curves through those eight points. The curves of the net passing through an arbitrary point form a pencil; we choose the pencil of curves passing through an arbitrary point J of j_n. In § 5 we have seen that in this pencil appears *one* curve possessing in J a ninth double point; therefore:

Each point of j_n *is the ninth double point of one of the curves contained in the net* $(\mathbf{r})$.

§ 8. We take an arbitrary triangle $O_1 O_2 O_3$ as triangle of coordinates; the locus of the double points of the net $\mathbf{r} \equiv w_6 + \lambda u^2_3 + + \mu v^2_3 = 0$ is then found by elimination of λ and μ out of the equations

$$\frac{dv}{dx_1} = 0, \quad \frac{dv}{dx_2} = 0 \text{ and } \frac{dv}{dx_3} = 0.$$

As equation of that locus we then find:

$$uv \left\{ \frac{dw}{dx_1} \left(\frac{du}{dx_2} \frac{dv}{dx_3} - \frac{du}{dx_3} \frac{dv}{dx_2} \right) + \frac{dw}{dx_2} \left(\frac{du}{dx_3} \frac{dv}{dx_1} - \frac{du}{dx_1} \frac{dv}{dx_3} \right) + \right.$$
$$\left. + \frac{dw}{dx_3} \left(\frac{du}{dx_1} \frac{dv}{dx_2} - \frac{du}{dx_2} \frac{dv}{dx_1} \right) \right\} = 0.$$

The factor uv in the first member of this equation means simply that each point of the curves u_3 and v_3 counting double can be regarded as a double point; as locus of the point J we find:

$$\frac{dw}{dx_1}\left(\frac{du}{dx_2}\frac{dv}{dx_3}-\frac{dv}{dx_2}\frac{du}{dx_3}\right)+\frac{dw}{dx_2}\left(\frac{du}{dx_3}\frac{dv}{dx_1}-\frac{du}{dx_1}\frac{dv}{dx_3}\right)+$$
$$+\frac{dw}{dx_3}\left(\frac{du}{dx_1}\frac{dv}{dx_2}-\frac{du}{dx_2}\frac{dv}{dx_1}\right)=0.$$

This equation of order nine represents the curve j_n which for the future we shall call j_9.

We now allow the vertex O_3 of the triangle of coordinates to coincide with D_1; the equations of the curves w_6, u_3, and v_3 are ranged according to the descending powers of x_3, written thus:

$$w_6 = x^4_3\,(ax^2_1 + 2bx_1\,x_2 + cx^4_2) + \ldots = 0$$
$$u_3 \equiv x^2_3\,(a'x_1 + b'x_2) + \ldots = 0$$
$$v_3 \equiv x^2_3\,(a''x_1 + b''x_2) + \ldots = 0$$

The first member of the equation representing the curve j_9 evidently possesses now no term in which x_3 appears to a lower power than the sixth; so D_1 is a triple point of j_9 and D_2, $D_3 \ldots D_8$ likewise.

§ 9. To the curves of order six possessing in D_1, $D_2 \ldots D_8$ double points belongs one degenerated into the line D_1D_2 and a curve of order five having in D_3, $D_4 \ldots D_8$ double points and passing moreover through D_1 and D_2. The latter is cut by D_1D_2 in three points more which must lie on j_9; thus on each of the lines connecting D_iD_k three points of j_9 can be indicated.

Let us suppose a conic D_1, $D_2 \ldots D_5$ and a quartic possessing in D_6, D_7 and D_8 double points and passing also through D_1, $D_2 \ldots D_5$; then these form together also a c_6 with double points in D_1, $D_2 \ldots D_8$; the remaining three points of intersection of the two curves lie on j_9. Thus on each of the 56 conics $D_iD_kD_lD_mD_n$ three points of j_9 are determined.

Each c_3 through D_1, $D_2 \ldots D_8$ cuts j_9 besides in these points in three points more; we have already seen how these points can be determined. We have also seen that B_9, the ninth base point of the c_3 pencil, does not lie on j_9; by allowing the vertex O_3 of the triangle of coordinates to coincide with B_9 we can easily deduce this out of the equation of j_9.

§ 10. Let w_6 be a curve of order six possessing in D_1, $D_2 \ldots D_9$ double points, whilst u_3 is the cubic through those points; then by

$\beta \equiv w_6 + \lambda u_3^2 = 0$ is represented a pencil (β) of curves of order six with nine double points. To a pencil of curves of order nine belong in general $3(n-1)^2$ curves possessing a double point; this amount must however be diminished by seven for each common double point which the curves possess in the base points. So we can expect that there will be twelve points, which can appear as tenth double point of a curve out of the pencil (β). It seems however desirable to prove that in this case too where one of the curves is a c_3 counting double the number of these points is twelve.

The points indicated are found by elimination of λ out of the equations:

$$\frac{d\beta}{dx_1} = 0\,,\quad \frac{d\beta}{dx_2} = 0 \text{ and } \frac{d\beta}{dx_3} = 0, \text{ or}$$

$$\frac{dw}{dx_1} + \lambda \frac{du}{dx_1} = 0\,,\quad \frac{dw}{dx_2} + \lambda \frac{du}{dx_2} = 0\,,\quad \frac{dw}{dx_3} + \lambda \frac{du}{dx_3} = 0.$$

By this elimination we find:

$$\frac{\dfrac{dw}{dx_1}}{\dfrac{du}{dx_1}} = \frac{\dfrac{dw}{dx_2}}{\dfrac{du}{dx_2}} = \frac{\dfrac{dw}{dx_3}}{\dfrac{du}{dx_3}}\,,$$

which equations represent three curves, whose common points of intersection — if only differing from the base points of (β) — are the demanded double points. (The factor $u = 0$, which we have omitted means that each point of u_3 can be regarded as a double point,

We write them in this form:

$$\frac{dw}{dx_1}\frac{du}{dx_2} - \frac{dw}{dx_2}\frac{du}{dx_1} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{dw}{dx_1}\frac{du}{dx_3} - \frac{dw}{dx_3}\frac{du}{dx_1} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\frac{dw}{dx_2}\frac{du}{dx_3} - \frac{dw}{dx_3}\frac{du}{dx_2} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The curves represented by (1) and (2) have forty-nine points of intersection; among these there are however ten which do not lie on (3), viz. the points which satisfy $\dfrac{dw}{dx_1} = 0$ and $\dfrac{du}{dx_1} = 0$. The remaining thirty-nine points must still be diminished by the points of intersection lying in D_1, $D_2 \ldots D_9$. If again we allow the vertex O_3 of the triangle of coordinates to coincide with D_1 and if we note down the equations of w_6 and u_3 ranged according to the descending powers of x_3 (see § 8), it is evident, that (2) and (3) possess in D_1 a double point, whilst (1) has in D_1 a single point; farthermore they have all three in D_1 a common tangent with the equation

$$x_1\,(ab'-a'b) + x_2\,(bb'-ac) = 0.$$

So in each of the base points of the pencil (β) lie three common points of intersection of (1), (2) and (3); besides $D_1, D_2 \ldots D_9$ the curves (1), (2) and (3) have $39 - 3 \times 9 = 12$ more common points So there are really 12 curves, possessing besides $D_1, D_2 \ldots D_9$ still a tenth double point.

We can directly indicate those twelve points. Each of those points must lie on the curve j_9, determined by $D_1, D_2 \ldots D_8$ and likewise on the curve j'_9, which is determined in the same way by $D_2, D_3 \ldots D_9$. These two curves have 81 points of intersection of which, however, nine lie in each of the points $D_2, D_3 \ldots D_8$ and three in each of the points D_1 and D_9. The remaining points are those indicated.

To a c_6-pencil with nine double points belong twelve curves possessing still a tenth double point.

§ 11. I wish to draw attention to another property of these points. If $P\,(x'_1, x'_2, x'_3)$ is an arbitrary point then the polar lines of P with respect to the curves out of the pencil (β) are represented by

$$x_1\left(\frac{dw}{dx_1} + \lambda u\,\frac{du}{dx_1}\right)_P + x_2\left(\frac{dw}{dx_2} + \lambda u\,\frac{du}{dx_2}\right)_P + x_3\left(\frac{dw}{dx_3} + \lambda u\,\frac{du}{dx_3}\right)_P = 0.$$

We shall now put the question whether it is possible to give P such a position that the polar line of P with respect to each curve out of the pencil is the same. Evidently for that it is necessary that the coordinates of P satisfy the equation $u = 0$, or the equations,

$$\frac{\dfrac{dw}{dx_1}}{\dfrac{du}{dx_1}} = \frac{\dfrac{dw}{dx_2}}{\dfrac{du}{dx_2}} = \frac{\dfrac{dw}{dx_3}}{\dfrac{du}{dx_3}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (I)$$

So P must be on u_3 or — as the system of equations (I) is the same as the system which we came across in § 10 — P must be one of the 12 points found there. Hence:

If $D_1, D_2 \ldots D_{10}$ are the double points of a rational curve of order six, then the polar line of one of these points with respect to the curves out of the c_6-pencil possessing the other nine as double points, is a fixed line.

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(Communicated in the meeting of November 26, 1910).

Δb positive.

24. Up to now we have considered the case Δb *negative.* Then the coexistence-curve liquid-solid proceeds from high pressure-values at $T=0$, with a maximum in the neighbourhood of $T=0$, either to a horizontal point of inflection E,D, at the same time *critical point liquid-solid,* where the two phases become identical, and where the minimum E of the isotherm coincides with the maximum D (see inter alia fig. 20 of V) — or to the neighbourhood of a horizontal point of inflection D,C, where the maximum D coincides with the minimum C.

In the example chosen by us, the first thing takes place when $-\Delta b < 0{,}454$; the second when $-\Delta b > 0{,}454$. For $-\Delta b = 0{,}454$, in the transition case, E, D, and C coincide all three.

For the intersection of the coexistence-curve of liquid-solid and that of vapour-liquid, so that a triple-point S arises, it is required that the said critical point E,D or the point of inflection D,C is found at a negative pressure, as the pressure in the triple point has mostly a very slight positive value. In our example e.g. this occurs for $-\Delta b = 0{,}5$ (fig. 14). Then S lies at about $^1/_4\ T_c$.

Now if Δb is *positive,* all this changes. Then the coexistence-curve ascends from below (see fig. 23—25) from low pressures, intersects in favourable cases (Δb large) the line vapour-liquid in a triple-point S, and again terminates in a *critical point* E,D solid-liquid. The curve, however, never terminates in a point of inflection D,C, as for Δb negative, when $-\Delta b > 0{,}454$. But it arises very low down from such a point [or rather in its neighbourhood, because only at somewhat higher temperature the first coexistence solid-liquid begins (see fig. 20 of V)].

So for Δb *negative* the course is *from* the axis $T=0$ to a critical point E,D or close to a point of inflection D,C (according to the value of $-\Delta b$), thus running from *above downward,* with (beyond the pressure maximum near $T=0$) always *negative* values of $\frac{dp}{dt}$; for Δb *positive,* on the other hand, *from* a point of inflection D,C to a critical point E,D, thus running *from below upward* always with *positive* values of $\frac{dp}{dt}$. For a definite value of Δb the two endpoints of this curve, which is limited on both sides in this way, will coincide (and accordingly also the *three* points E, D, and C), and the whole coexistence-curve reduces to a single point (fig. 26).

We shall prove the above in the following paragraphs.

25. In the first place it may be observed that the equation of dissociation:

$$\frac{\beta^2}{1-\beta^2} = \frac{c\,T^{\gamma+1}\,e^{-\frac{q_0}{RT}}\,e^{-\frac{(p+a/v^2)\Delta b}{RT}}}{p+a/v^2} \quad . \quad . \quad . \quad . \quad . \quad (a)$$

now gives rise to an altogether different shape of $\beta = f(v)$ for T constant. If Δb is negative, the course is as in fig. 21, with a minimum in M; for Δb positive the course is indicated by fig. 22. This is at once evident when $p + a/v^2$ is replaced by $\frac{(1+\beta)RT}{v-b}$ in the above equation, by which it becomes:

$$\frac{\beta^2}{1-\beta} = c\,R\,T^{\gamma}\,e^{-\frac{q_0}{RT}}\,e^{-\frac{(1+\beta)\Delta b}{v-b}}\,(v-b) \quad . \quad . \quad . \quad (b)$$

For Δb negative the value of β will approach unity both for $v = b$ and for $v = \infty$; whereas for Δb positive for $v = b$ the value of β approaches zero on account of the exponential factor, which then becomes $e^{-\infty}$. The transition of β from 1 (liquid state) to near 0 (solid state) takes place in the *descending* portion AB for Δb negative (fig. 21); on the other hand the transition of β from 0 (solid state) to near 1 (liquid state) will take place in the *ascending* part AB for Δb positive (fig. 22). As we saw in the preceding papers, the increase of β from the minimum M to 1 again, takes place for Δb negative in the vapour phase and large values of v.

Now for Δb positive the change between A and B (fig. 22) will take place for small volumes only, when q_0 is not too large. For else evidently in consequence of the small value of the exponential factor $e^{-\frac{q_0}{RT}}$ — the index of which has now no longer the reversed sign of that of $-\frac{(p+a/v^2)\Delta b}{RT}$, but the same — the nearly asymptotic course of OA will continue to the neighbourhood of great values of v, and the change of β will take place between A and B in the *vapour phase.* But this evidently prevents the isotherm from twice taking a turn (in consequence of the rapid decrease of a/v^2 (from the value $\frac{a}{b_1^2}$ to the value $\frac{a}{(2\,b_2)^2}$) between the volumes $v=b_1$ (solid) and

$v = 2b_2$ (liquid), which gives rise to the coexistence solid-liquid. In other words there is no value of Δb for which a coexistence-curve solid-liquid will occur.

This is immediately seen, when we e. g. assume $q_0 = 3200$, as in our former example for Δb negative.

If we now namely put (equation I p. 773)

$$\frac{p + {}^a/_{v^2}}{RT}\,\Delta b = \varphi \quad ; \quad \frac{RT}{q_0} = \theta \quad ; \quad \frac{c q_0^{\gamma}}{R^{\gamma+1}}\,\Delta b = \lambda\,, \quad . \quad . \quad . \quad (c)$$

(a) passes into:

$$\frac{\beta^2}{1-\beta^2} = \lambda\theta^{3/2}\, e^{-1/\theta}\ \frac{e^{-\gamma}}{\varphi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (d)$$

This agrees entirely with the preceding form, except that now $e^{-\gamma}$ occurs and not e^{γ}. With $\Delta b = 0,5$ and $T = 9$ (see I p. 774) we now find:

$$log^{10}\,\frac{\beta^2}{1-\beta^2} = -\ 76,077 - 0,4343\ \varphi - log^{10}\ \varphi,$$

with the same values of a, b_1, c, and q_0 as in our preceding papers. In this equation $-0,4343\ \varphi$ occurs instead of $+\ 0,4343\ \varphi$. But in consequence of this not before $\varphi = 10^{-74}$ the value of $log^{10}\,\frac{\beta^2}{1-\beta^2}$ will become such that β begins to move away from 0 (the point A in fig. 22), viz. $= -\ 2,077$; while at $\varphi = 10^{-78}$ the value of log^{10} rises to 1,923, and β gets in the neighbourhood of 1 (the point B in the same figure). But in consequence of the formula $v = b + (v-b)$, i. e. $v = (b_1 + \beta\Delta b) + \frac{1+\beta}{\varphi}\,\Delta b$, or (cf. formula (5) on p. 773)

$$v = b_1 + \left(\beta + \frac{1+\beta}{\varphi}\right)\Delta b\,, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (e)$$

v will then be of the order 10^{74}, resp. 10^{78}.

Even at $T = 100$, in consequence of which

$$log^{10}\,\frac{\beta^2}{1-\beta^2} = -\ 4,250 - 0,4343\ \varphi - log^{10}\ \varphi\,,$$

the portion AB evidently lies between $\varphi = 10^{-2}$ and 10^{-6}, i. e. v between 50 and 10^6 (in the first case β is namely $= 0$, in the second $= 1$), so at much too large volumes.

Not before $T = 200$ the change of β from 0 to 1 would be found between values of v which might deserve consideration — but then we have already arrived above the critical temperature vapour-liquid, which lies at 133° for $\Delta b = 0,5$.

So we are obliged to lower the value of q_0 in such a way that the value of λ becomes considerably smaller. If e. g. we take q_0 a hundred times smaller than in our former example, i. e. $q_0 = 32$, we have the following values ($\Delta b = 0{,}5$):

$c = 2$, $q_0 = 32$ (both Gr. Cal.) $b_1 = 1$, $2b_2 = 1{,}5$, $a = 2700$.

The value of $2b_2 = b_1 + \Delta b$ (liquid) is now not $1 - 0{,}5 = 0{,}5$, but $1 + 0{,}5 = 1{,}5$, i. e. greater than that of b_1 (solid). The critical temperature (vapour-liquid) is found from:

$$(1 + \beta)\, RT_c = \frac{8}{27}\, \frac{a}{2b_2}\,,$$

assuming that for T_c all the double molecules are dissociated, hence b has become $= 2b_2$. This gives ($\beta = 1$) $4T_c = \frac{8}{27} \times \frac{2700}{1^1/_2} = \frac{1600}{3}$, so:

$$T_c = \frac{400}{3} = 133^1/_3\,.$$

In our former example, where $\Delta b = -{}^1/_2$, and so $2b_2 = {}^1/_2$, T_c was $= 400°$.

The critical pressure now is $p_c = \frac{1}{27}\frac{a}{(2b_2)^2} = \frac{1}{27} \times \frac{2700}{2^1/_4} = \frac{400}{9} = 44^4/_9$, instead of 400 for $\Delta b = -0{,}5$.

26. Now we proceed to the more accurate calculation of the coexistence-curve solid-liquid for

$$\Delta b = 0{,}5 \;\; (b_1 = 1,\; 2b_2 = 1{,}5),$$

indicated in fig. 23.

The successive isotherms, belonging to the different points of the curve *PQSRCr* in fig. 23, are represented in the figures 27—32. In fig. 27 the stage below the point *P*, where coexistence vapour-solid is only possible (on the line *OS* of fig. 23). In fig. 28 the point of inflection *D,C* appears (*P* in fig. 23), and somewhat later (fig. 29) the first coexistence liquid-solid (the point *Q* in fig. 23). As this, however, takes place at negative pressures, the said coexistence is not realisable, and for the present only the coexistence vapour-solid is found as in fig. 27 and 28.

Only at still higher temperature (e. g. the point *R* in fig. 23) the coexistence liquid-solid has become realisable (and this already starting from the triple point *S*), which is represented in fig. 30. Now we have at first vapour-liquid, and at higher pressures liquid-solid. In fig. 31 the *critical point* liquid-solid (*Cr* in fig. 23) appears, after which (fig. 32) no coexistence liquid-solid is possible any more. Then only vapour-liquid remains — till at last this too disappears at the usual critical temperature (vapour-liquid).

Also in the figures 24, 25, and 26 these stages are passed through in quite the same succession; only everything is more compressed then, that is, the distance between the points P and Cr becomes smaller and smaller, and the coexistence-curve will at last quite disappear from the field (fig. 26).

Let us now calculate $\underline{T = 50}$ for $\Delta b = 0{,}5$ (fig. 28). The value of λ (cf. the formula (c)) is $= 32$. Further θ is $= \frac{25}{8}$, so that (d) passes into

$$log^{10} \frac{\beta^3}{1-\beta^2} = 2{,}109 - 0{,}4343\varphi - log^{10}\varphi .$$

Then the values of v are calculated from (e), i. e.:

$$v = 1 + 0{,}5\left(\beta + \frac{1+\beta}{\varphi}\right),$$

and those of p from (compare (4) on p. 773 loc. cit.):

$$p = \frac{RT}{\Delta b}\varphi - \frac{a}{v^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (f)$$

i. e. here from

$$p = 200\varphi - \frac{2700}{v^2} .$$

This gives the following survey.

$T = 50$

φ	log^{10}	β	v	a/v^2	p
8	4.377	0.073	1.104	2217	—617
7	3.885	0.128	1.145	2029	—629
6	3.384	0.225	1.214	1832	—632 (E)
5	2.871	0.384	1.330	1526	—526
4	2.339	0.609	1.505	1192	—392
3	1.780	0.825	1.717	916	—316
2	1.170	0.947	1.960	703	—303
1	0.434	0.990	2.490	435	—235

So the temperature of the point of inflection D,C lies somewhat above 50°, viz. at $\underline{T = 52{,}3}$ ($p_{D,C} = -282$).

For $\underline{T = 60,}$ for which $\theta = \frac{15}{4}$,

$$log^{10} \frac{\beta^2}{1-\beta^2} = 2{,}250 - 0{,}4343\varphi - log^{10}\varphi \quad ; \quad p = 240\varphi - \frac{2700}{v^2},$$

holds, from which we calculate:

$T = 60$

φ	log^{10}	β	v	a/v^2	p
8	—2.127	0.086	1.111	2188	—268
7	—1.635	0.150	1.157	2016	—336 (*E*)
6	—1.134	0.262	1.236	1767	—327
5	—0.621	0.440	1.364	1451	—151
4	—0.089	0.670	1.544	1133	—173
3	+0.470	0.864	1.743	889	—169 (*D*)
2	1.080	0.961	1.971	695	—215 (*C*)
1	1.816	0.992	2.492	435	—195

A maximum has appeared at *D* and a minimum at *C*, but no coexistence pressure as yet, because the pressure-curve about halfway *E* and *D* ($p = \pm - 250$) still runs below *C*. (Fig. 29).

So let us repeat the calculation for $\underline{T = 65}$. Here $\theta = \frac{65}{16}$, and with

$$log^{10} \frac{\beta^2}{1-\beta^2} = 2{,}311 - 0{,}4344\varphi - log^{10}\varphi \quad ; \quad p = 260\varphi - \frac{2700}{v^2}$$

we get the following survey:

$T = 65$

φ	log^{10}	β	v	a/v^2	p
7	—1.574	0.161	1.164	1992	—172
6	—1.073	0.279	1.246	1739	—179 (*E*)
5	—0.560	0.465	1.379	1419	—119
4	—0.028	0.696	1.560	1110	— 70 (*D*)
3	+0.531	0.879	1.752	879	— 99
2	1.141	0.966	1.974	693	—173
1	1.877	0.993	2.493	435	—175 (*C*)
0.5	2.395	0.998	3.497	221	— 91

The coexistence-pressure liquid-solid is about — 125; and it is real, because now — 125 is greater than the pressure in *C*. Hence the case of fig. 29 lies between 60° and 65°. By interpolation we easily calculate that the pressure of coexistence (fig. 29) first makes its appearance at $\underline{62°}$, where then $p = p_C$ is about $= \underline{-200.}$

Now this pressure is real, but still unrealisable as negative pressure.

Now we calculate the isotherm of $T = 70$. Here $\theta = \frac{35}{8}$, and further:

$$log^{10} \frac{\beta^2}{1-\beta^2} = 2{,}367 - 0{,}4343\varphi - log^{10}\varphi \quad ; \quad p = 280\varphi - \frac{2700}{v^2},$$

from which the following table is drawn up.

$T = 70$

φ	log^{10}	β	v	a/v^2	p
7	—1.518	0.172	1.170	1972	— 12
6	—1.017	0.296	1.256	1711	— 31 *(E)*
5	—0 504	0.488	1.393	1392	+ 8
4	+0.020	0.718	1.574	1090	+ 30 *(D)*
3	0.587	0.891	1 761	871	— 31
2	1.197	0.970	1.977	691	—131
1	1.933	0.994	2.494	434	—154 *(C)*
0.5	2.451	0.998	3.497	221	— 81

The pressure of coexistence liquid-solid is about $p = 0$, so that we have reached the triple point S (fig. 23), and from this moment the mentioned pressure becomes realisable.

Now $T = 75$ (fig. 30) must be calculated for the determination of the point Cr (fig. 23). With $\theta = \frac{75}{16}$ we get:

$$log^{10} \frac{\beta^2}{1-\beta^2} = 2{,}419 - 0{,}4343\varphi - log^{10}\varphi \quad ; \quad p = 300\varphi - \frac{2700}{v^2}.$$

This yields:

$T = 75$

φ	log^{10}	β	v	a/v^2	p
7	—1.466	0.182	1.175	1955	145
6	—0.965	0 313	1.266	1684	116 *(E)*
5	—0.452	0.511	1.406	1366	134 *(D)*
4	+0.080	0.739	1.587	1072	128
3	0.639	0.902	1.768	864	36
2	1.249	0.973	1.979	689	— 89
1	1.985	0.995	2.495	434	—134 *(C)*
0.5	2.503	0.998	3.497	221	— 71

So the coincidence of E and D in a *critical point* solid-liquid will take place somewhat above 75°.

Finally we calculate $T=80$ (fig 31) for this purpose. Then $\theta=5$ and

$$log^{10}\frac{\beta^2}{1-\beta^2}=2,467-0,4343\varphi-log^{10}\varphi \quad ; \quad p=320\varphi-\frac{2700}{v^2},$$

which gives rise to the following table.

$T=80$

φ	log^{10}	β	v	a/v^2	p	
7	—1.418	0.192	1.181	1935	305	
6	—0.917	0.229	1.275	1661	259	E,D
5	—0.404	0.532	1.419	1341	259	
4	+0.128	0.757	1.598	1057	223	
3	0.687	0.911	1.774	858	102	
2	1.297	0.976	1.982	687	— 47	
1	2.033	0.995	2.495	434	—114	C
0.5	2.551	0.998	3.497	221	— 61	

So the coincidence takes place at exactly 80°.

If we now examine the foregoing tables, it appears (see fig. 23), that the whole curve of coexistence solid-liquid extends from $T=62$, $p=-200$ (the point Q) to $T=80$, $p=259$ (the point Cr). Only the part above S, ($T=70$), $p=0$), however, is realisable.

The triple-point S lying at 70°, and the critical temperature vapour-liquid being $=133°$, we have here:

$$\frac{T_0}{T_c}=\frac{70}{133}=0,53,$$

which is in perfect harmony with the value which was found for it in many cases.

We remind the reader that for this relation (provided T_0 does not lie too near any critical point) the general equation [see V, p. 461, formula (27*a*)]:

$$\frac{T_0}{T_c}=\frac{27}{8}\left(\frac{-\Delta b}{b_1}\right)^2 : log\left(\frac{b_1^2}{4b_2^2}\cdot\frac{1}{2\beta'}\right)$$

holds.

With $\Delta b=0,5$, $b_1=1$, $b_2=1,5$ this becomes:

$$\frac{T_0}{T_c}=\frac{27}{32} : log\left(\frac{2}{9\beta'}\right)$$

For this we find the value 0,5, when $\frac{2}{9\beta'} = 5{,}5$, i.e. $\beta' = 0{,}04$, which is a very plausible value.

When the value of Δb diminishes, also the value of $T_0 : T_c$ becomes slightly less, but remains in the neighbourhood of 0,5. But as we shall immediately see, the whole of the coexistence-curve liquid-solid has come below $p=0$, already for $\Delta b = 0{,}4$, and so it is no longer realisable — at least with the values of b_1, Δb, etc. assumed by us.

This will appear from the tables following here, which hold for $\Delta b = 0{,}4$.

27. We shall calculate the isotherms of 50°, 60°, and 70° for the case (see fig. 24)

$$\underline{\Delta b = 0{,}4} \quad (b_1 = 1,\ 2b_2 = 1{,}4).$$

The value of λ is then $= 25{,}6$. The critical data are $T_c = 143°$, $p_c = 51$ (cf. § 25; $2b_2$ is then namely $= 1{,}4$).

For $\underline{T = 50}$ we have $\theta = \frac{25}{8}$, and the formula (d) passes into

$$log^{10} \frac{\beta^2}{1-\beta^2} = 2{,}012 - 0{,}4343\,\varphi - log^{10}\,\varphi,$$

while

$$v = 1 + 0{,}4\left(\beta + \frac{1+\beta^2}{\varphi}\right) \quad ; \quad p = 250\,\varphi - \frac{2700}{v^2}.$$

In consequence of this we get:

$T = 50$

φ	log^{10}	β	v	a/v^2	p
7	−1.873	0.115	1.110	2193	−443
6	−1.372	0.202	1.161	20 4	−504 (*E*)
5	−0.859	0.348	1.247	1735	−485
4	−0.327	0.566	1.383	1412	−412
3	+0.232	0.794	1.557	1114	−364 (*D*)
2	0 842	0.935	1.761	871	−371 (*C*)
1	1 578	0.987	2.190	563	−313

For $\underline{T = 60}$ we have $\theta = \frac{15}{4}$, and further:

$$log^{10}\frac{\beta^2}{1-\beta^2}=2{,}154-0{,}4343\,\varphi-log^{10}\,\varphi\quad;\quad p=300\,\varphi-\frac{2700}{v^2}\,,$$

from which we calculate:

$T=60$

φ	log^{10}	β	v	$a/_{v^2}$	p
7	—1.731	0.135	1.119	2156	— 56
6	—1.230	0.236	1.177	1951	—151
5	—0.717	0.401	1.273	1668	—168 *(E)*
4	—0.185	0.628	1.414	1250	—150 *(D)*
3	+0.374	0.838	1.580	1081	—181
2	0.984	0.952	1.771	861	—261
1	1.720	0.991	2.193	562	—262 *(C)*
0.5	2.238	0.997	2.996	301	—151

So the coincidence D,C lies just before 50°, and the first appearance of the pressure of coexistence between 50° and 60°. By interpolation we find easily the value $T=49$ ($p=-382$) for the point P (cf. fig. 28), and the value $T=54$ ($p=p_c=-327$) for the point Q (comp. also fig. 29).

Now we have still to calculate $T=70$ for the calculation of the point Cr. For this $\theta=\frac{35}{8}$, and we have:

$$log^{10}\frac{\beta^2}{1-\beta^2}=2{,}271-0{,}4343\,\varphi-log^{10}\,\varphi\quad;\quad p=350\,\varphi-\frac{2700}{v^2}\,,$$

which gives rise to the following table.

$T=70$

φ	log^{10}	β	v	$a/_{v^2}$	p
7	—1.614	0.154	1.128	2123	+327
6	—1.113	0.267	1.191	1903	+197
5	—0.600	0.448	1.295	1610	+140
4	—0.068	0.679	1.439	1303	+ 97
3	+0.491	0.869	1.597	1059	— 9
2	1.101	0.963	1.778	855	—155
1	1.837	0.993	2.194	561	—211 *(C)*
0.5	2.355	0.998	2.998	300	—125

So in this case (compare fig. 32) we are far beyond the coincidence E, D. But by interpolation between 60° and 70° we find for $T = 63$:

$$
\begin{array}{rccccccc}
{}^a/_{v^2} = & 2146 & 1937 & 1651 & 1336 & 1074 & 859 & 562 \\
315\,\varphi = & 2205 & 1890 & 1575 & 1260 & 945 & 630 & 315 \\
p = & 59 & -47 & \underbrace{-76 \quad -76}_{E,D} & & -129 & -229 & \underset{C}{-247}
\end{array}
$$

so that the said coincidence takes place at $\underline{T = 63}$ ($p_{E,D} = -76$).

So we see that the whole coexistence-curve solid-liquid falls in the region of negative pressures, from $T = 54$, $p = -327$ to $T = 63$, $p = -76$. Accordingly the coexistence-curve vapour-liquid OK is *not* intersected by that for solid-liquid, and there exists *no solid state*.

If for $\Delta b = 0{,}5$ the line QCr extended from 62° to 80°, i.e. over a region of 18°, now it has contracted for $\Delta b = 0{,}4$ to a region of only 9°, viz. from 54° to 63°.

28. Let us now calculate the case (see fig. 25)

$$\underline{\Delta b = 0{,}3} \quad (b_1 = 1,\ 2b_2 = 1{,}3)$$

The whole curve lies between 40° and 50°, and so we determine the values of p for these two temperatures. The value of λ is now $= 19{,}2$; further $T_c = 154$, $p_c = 59$.

For $\underline{T = 40}$ we have $\theta = {}^5/_2$, and therefore:

$$log^{10} \frac{\beta^2}{1-\beta^2} = 1{,}706 - 0{,}4343\,\varphi - log^{10}\,\varphi$$

$$v = 1 + 0{,}3\left(\beta + \frac{1+\beta}{\varphi}\right); \qquad p = 266{,}7\,\varphi - \frac{2700}{v^2}$$

From this we find:

$T = 40$

φ	log^{10}	β	v	${}^a/_{v^2}$	p
6	—1.678	0.143	1.100	2231	—631
5	—1.165	0.253	1.151	2038	—705 *(E)*
4	—0.663	0.435	1.238	1761	—694
3	—0.074	0.677	1.371	1436	—636
2	+0.536	0.880	1.546	1130	—597
1	1.272	0.974	1.884	761	—494

For $\underline{T = 50}$ we have $\theta = \frac{25}{8}$, and further:

$$log^{10} \frac{\beta^2}{1-\beta^2} = 1{,}887 - 0{,}4343\,\varphi - log^{10}\,\varphi\ ; \ p = 333{,}3\,\varphi - \frac{2700}{v^2}.$$

from which the following table can be drawn up.

$T = 50$

φ	log^{10}	β	v	a/v^2	p	
6	—1.497	0.176	1.112	2183	—183	
5	—0.984	0.306	1.170	1982	—305	
4	—0.452	0.511	1.267	1683	—350	}
3	+0.107	0.749	1.400	1378	—378	}
2	0.717	0.916	1.562	1107	—440	*(C)*
1	1.453	0.983	1.890	756	—423	

For 40° (cf. fig. 27) the point of inflection D,C (fig. 28 has not yet been reached; for 50° (fig. 32) we are already far beyond the coincidence E,D (fig. 31).

Now we find by interpolation:

$T = 44$

$$p = 293,3\,\varphi - \frac{2700}{v^2}$$

φ	a/v^2	p	
6	2212	—452	
5	2012	—545	
4	1730	—557	*(E)*
3	1413	—533	} *D,C*
2	1121	—534	}
1	759	—466	

$T = 45$

$$p = 300\,\varphi - \frac{2700}{v^2}$$

φ	a/v^2	p	
6	2207	—407	
5	2005	—505	
4	1722	—522	*(E)*
3	1407	—507	*(D)*
2	1119	—519	*(C)*
1	758	—459	

$T = 46$

$$p = 306,7\,\varphi - \frac{2700}{v^2}$$

φ	a/v^2	p	
6	2202	—362	
5	1998	—465	
4	1714	—487	*(E)*
3	1401	—481	*(D)*
2	1116	—503	*(C)*
1	758	—451	

$T = 47$

$$p = 313,3\,\varphi - \frac{2700}{v^2}$$

φ	a/v^2	p	
6	2197	—317	
5	1992	—425	
4	1706	—453	}
3	1395	—455	}
2	1114	—487	(C)
1	757	—444	

It appears from these tables that the coincidence D,C now takes place at $T=44$ ($p_{D,C}=-534$). Further that the first pressure of coexistence liquid-solid (fig. 29) appears at $T=44,7$ ($p=p_C=-524$). For then we have with $p=298\varphi-\frac{2700}{v^2}$, resp. for $\varphi=4$, 3 and 2:

$a/v^2=$	1724,4	1408,8	1119,6
$p=$	$-532,4$	$-514,8$	$-523,6$
	E	D	C

so that the pressure of coexistence is about 523,6, p_C also having this value.

Finally it appears that the coincidence E,D takes place at $T=46,7$ ($p_{E,D}=-463$). For then we have resp. for $\varphi=4$ and 3:

$$a/v^2=1708,4 \text{ and } 1396,8 \quad ; \quad p=463,1 \text{ and } 462,8.$$

So in the case $\Delta b=0,3$ the whole coexistence-curve only stretches over an interval of 2° viz. from 44°,7 to 46°,7, again in the region of negative pressures, hence not realisable.

29. It is now easy to derive that the coexistence-curve entirely disappears from the field for

$$\Delta b=0,276 \;(T_c=157,\; p_c=61).$$

Then for

$$T=43, \quad p=-570$$

the end-points P and Cr coincide, and in the isotherm of 43° the points E, D, and C coincide to a contact of higher order.

For $\Delta b=0,4$ the difference of temperature between the end-points P and Cr amounts to 14°, whereas this is only 2°,7 for $\Delta b=0,3$. By interpolation we find from this that the difference 2°,7 has been reduced to 0 for $\Delta b=0,3-0,24\,(0,4-0,3)$, i.e. for 0,276. Then $T_{D,C}=T_{E,D,C}=44-0,24\times 5=42,8$, while $p_{D,C}=p_{E,D,C}=$ $=-534-0,24\times 152=-570$.

If we finally comprise everything found for Δb positive in one table, we get the following summary.

$\Delta b=0.5$	0.4	0.3	0.276
$T_P=52.3$ ($p=-282$)	49 (−382)	44 (−534)	42.8 (−570)
$T_Q=62$ ($p=-200$)	54 (−327)	44.7 (−524)	
$T_{Cr}=80$ ($p=+259$)	63 (− 76)	46.7 (−463)	

So just as for Δb negative (see our preceding paper) we have a realisable coexistence-curve liquid-solid, viz. with *positive* pressures above a *triple-point* S, for Δb positive only when $\angle b$ has a sufficiently high value (here $=0,5$). For Δb positive this triple-point lies at about $^1/_2\ T_c$, in accordance with what was found experimentally for many substances.

In how far these results are still subject to modification, when not — as was supposed up to now — *two* simple molecules associate to one complex molecule, but more than two, we shall have to discuss in a concluding paper. Moreover some remarks will be made about some papers by VON WEIMARN, who lately also concluded to the improbability of the TAMMANN melting-point curve on the ground of crystallographic-molecular considerations, and who then already stated the *probable* existence of a critical point solid-liquid, which existence, however, has only been raised beyond doubt by our theoretical considerations.

Physiology. — *"On the negative variation of the nervus acusticus caused by a sound."* By F. J. J. BUIJTENDIJK. (Communicated by Prof. H. ZWAARDEMAKER).

(Communicated in the meeting of November 26, 1910).

Up till now of the electric phenomena caused by the natural irritation of the organs, only those of the retina and of the nervus opticus have been investigated. [1]

As I have been told, about 1904 a French investigator observed electric currents with a mirror galvanometer, when he connected this measuring apparatus with the nervus acusticus of a rabbit and a loud sound struck the ear of the experimental animal.

With the string-galvanometer of EINTHOVEN I succeeded in registrating the action-currents of the nervus acusticus suggested by a natural irritation. Under ether-narcosis of the experimental animal, electrodes of a specific form were placed by means of a trepanation opening into the hindmost skull-cavity of a cavia. These electrodes, a thin metallic tube, containing an isolated metallic pin were pushed on along the side-parietes of the cerebellum, usually after piercing the juncture of the flocculus with the rest of the cerebellum. In this way a trial was made to reach the nervus acusticus with the extremity

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[1] Vide a. o. EINTHOVEN and JOLLY. Quart. Journal of Experim. Physiol. Volume I. 1908 page 373.

of the metallic pin, projecting about $^1/_2$ cm out of the surrounding electrode. A comparison of the results of these experiments with the section of the animals used, proved that the strongest action currents were obtained when the electrode had reached the spot where the nervus acusticus enters into the medulla longata or the adjoining part of the medulla oblongata (tuberculum acusticum). The electrodes were now united with the string-galvanometer and a compensation apparatus (composed according to the method of WERTHEIM SALOMONSON[1]). Thereupon a percussion was fired with a pistolet, and the motion of the string simultaneously with a signal, stating the moment of the shot, was registered by photography. The oscillation that the string showed, appeared to correspond with a current of 4.5×10^{-8} to 9×10^{-9} ampère.

In the various experiments the latent period had a duration of 0.003—0.005 seconds.

The form of the obtained curve variegated in the various experiments; in the same experiment, however, the form remained pretty well constant. Without exception a deviation of the string had a two- or more-phasical character. Sometimes the phases passed imperceptibly into each other (vide fig. II), at other times, a more or less distinct pause was perceptible (vide fig. I). Moreover the string showed a very slight oscillation with a frequency of 1000—1500 per second. By the control-experiments this oscillating motion was proved not to be a physiological phenomenon. The object of these controlling experiments was to ascertain in how far the oscillations of the galvanometer were not caused by the action-current of the nervus acusticus. In the first place it appeared that, with opened current-chain, the string showed no oscillation when the shot resounded; the above-mentioned slight oscillation did appear with a latent period shorter than 0.001 second. Further it appeared that by putting various spots of the upper- or lower-brain out of circuit, the string showed no oscillation. Motions of the animal were entirely excluded by curarisation, the respiration-motions were also suspended. If one left the electrodes in situ, and waited, without altering anything in the experimental composition, till the animal had died and entirely cooled down, even the strongest report could no longer produce any oscillation in the string, the resistance in the chain however not having increased.

If an experiment was made when the animal was dead but had not yet entirely cooled down, an oscillation was still to be obtained though considerably inferior to the one resulting from the living

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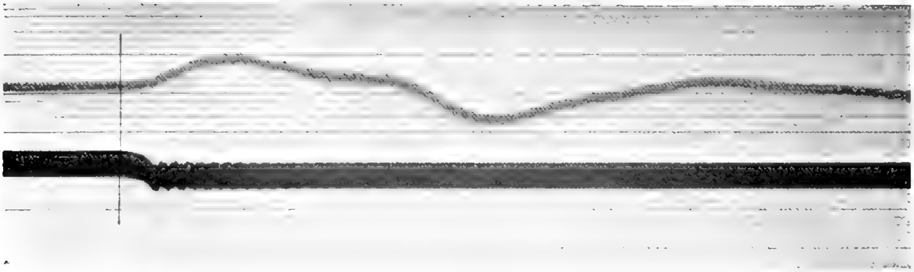
[1] WERTHEIM SALOMONSON. Zeitschr. f. Biol. Techn. 1909 Volume 1, page 366.

F. J. J. BUYTENDIJK. "On the negative variation of the nervus acusticus caused by a sound."



on the line of the abscesses 1 mm is equal to $\frac{1}{1250}$ second, on the ordinate 1 mm is equal to $6,1 \times 10^{-9}$ ampère.

Fig. I.

on the abscis 1 mm is equal to $\frac{1}{1250}$ second, on the ordinate 1 mm is eq al to $6,1 \times 10^{-9}$ ampère.

Fig. II.

Fig. I and Fig. II: Electric phenomenon in the nervus acusticus of the cavia caused by a reporting sound

animal. Moreover the latent period had considerably increased and amounted to about 0.015 second. A comparison of the curves with those of the electric phenomena of the eye can, in my opinion, not be made, as the string of the galvanometer in my experiments had a very slight tension, and the curves consequently would require much rectification, in order to indicate the oscillations of the current that occur in reality.

For the latent period Einthoven and Jolly (l.c.) found for the frog's eye as the smallest value 0.01 second, moreover they report that for the stronger irritations the latent period is considerably shorter than for the feebler.

Perhaps there is some connection between the very short latent period, found in my experiments, and the exceedingly strong irritation which the impulsive sound of the report is for the experimental animal. Received by the microphone the report seemed to give an amplitude of oscillation of the string when brought into circuit with the secondary chain, forty times greater than a very strong flute-tone (a^3 — a^4).

I could however when blowing this flute and likewise with the sound of a clock, observe an oscillation of the string, when it was connected with the nervus acusticus of the experimental animal. The oscillation was very slight 1—2 mm. and appeared to remain constant during the flute-tone.

With the cavia it was utterly impossible for me to reach the nervus acusticus operatively. With the rabbit I could reach the nervus acusticus through the roof of the hindmost skull-cavity, by cutting away part of the cerebellum. By cauterization the violent hemorrhage had to be stopped. With a blunt hook the medulla was a little removed, and a platinum electrode was placed at a distance of ± $^1/_2$ cm. into the medulla oblongata. Now I could likewise register by photography an oscillation, though not so strong as at the stabbing experiments with the cavia, it was of about equal strength as the oscillation that the string shows, when the stabbing electrodes are applied to the rabbit.

There is still a third method for observing electric phenomena of the nervus of a cavia or a rabbit. Of two unpolarisable electrodes, one was placed in the porus acusticus internus, the other on an indifferent spot of the hindmost skull-cavity.

This was done under strong ether narcosis, the skull having been widely opened, and the whole mass of brain removed. In the dying animal very distinct electric currents were still observed in the nervus acusticus when the report struck the ear. As has already been remarked these oscillations were remarkably smaller and had greater latency.

I have likewise tried to conduct the active current of the nervus acusticus of the frog. The nervus acusticus of this experimental animal can easily be reached without injuring the normal circulation or the brain. I have however not succeeded in observing an oscillation of the string-galvanometer. This may be partly attributed to the insufficient sensibility of the instrument, on the other hand the sensibility of the frog for sounds is exceedingly trifling. A frog poisoned with strychnine which showed symptoms of spasms when being blown, did still react with muscular spasms at a shot in the immediate vicinity, but did not do so when the shot was fired at some distance. Of the different tones it was those of a low vibrating figure that caused the greater reaction upon such like frogs, the high tones often had no influence at all. From the experiments of YERKES [1]) about the vigorating influence of the tone on the effect of a mechanical irritation it appears that vibrations of 50—10000 per second, in some way or other, cause an irritation to the nervous system of the frog.

I can moreover communicate that like PIPER [2]) I could show an electric current in a pike with the string-galvanometer when with a glass-rod the otolith was moved. The unpolarisable electrodes were placed in such a way that one of them touched the nervus acusticus at the parietes of the emptied skull cavity, the other stood at some indifferent point of this parietes. Care was taken that neither the electrode nor the object could move from their places. I could not observe any electric action caused by a sound of whatever nature that was conveyed by the air to the head of the pike.

Mathematics. — *"On quartic curves of deficiency zero with a rhamphoid cusp and a node."* By Prof. GEORGE MAJCEN of Agram. (Communicated by Prof. JAN DE VRIES).

1. We shall here consider the quartic curve, which has as equation

$$(mx_3{}^2 + nx_1x_2)^2 - x_2x_3{}^2\,(a^2x_2 - bx_3) = 0 \quad . \quad . \quad . \quad . \quad (k_4)$$

It is easy to prove, that the represented curve has a rhamphoid cusp in the vertex $A\,(1,0,0)$ of the triangle of reference, that the cuspidal tangent is the side $x_2 = 0$ of this triangle, and that the vertex $B\,(0,1,0)$ is a node of the curve. The side $x_1 = 0$ is chosen

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[1]) YERKES Journ of Comp. neurol and Psychol XV, p. 279.

[2]) PIPER. Zentralblatt f. Physiol 1906 Bd. I, p. 293.

as the harmonic conjugate of $x_3 = 0$ with respect to the two tangents of the double point B.

Indeed, the first polar curve of the point A with respect to k_4 breaks up into $x_2 = 0$ and the conic

$$mx_3^2 + nx_1x_2 = 0,$$

which has in the vertex A five points in common with k_4. Evidently the only simple tangent of k_4, passing through the cusp A, is represented by

$$a^2x_2 - bx_3 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (t)$$

The equation of a conic, which touches k_4 on $x_2 = 0$ in the cusp A and still in two other points, can be written in the well known form:

$$x_3^2 + 2\varepsilon\,(mx_3^2 + nx_1x_2) + \varepsilon^2x_2\,(a^2x_2 - bx_3) = 0.$$

If such a conic degenerates into two straight lines, one of which will be the tangent $x_2 = 0$, then the other must be the only double tangent belonging to k_4.

If we put $2m\varepsilon = -1$, it follows from the last equation

$$x_2 = 0, \quad 4mnx_1 - (a^2x_2 - bx_3) = 0 \quad . \quad . \quad . \quad . \quad . \quad (d)$$

and we have the equation of the *double tangent* d.

From the form of this equation is evident, that the double tangent passes through the point of intersection of the lines

$$x_1 = 0 \text{ and } a^2x_2 - bx_3 = 0.$$

We can now say: The line (BR) joining the double point (B) to the point (R) of intersection of the double tangent with the simple tangent (t), passing through the cusp (A), is the *harmonic conjugate* of the line AB with respect to the two tangents of the double point B.

2. A pencil of conics having the two common tangents $x_2 = 0$, $x_1 = 0$, with the points of contact A and B respectively, is indicated by the equation

$$x^2_3 + \mu x_1x_2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Each of these conics cuts the curve k_4 moreover in two points M, N; let us determine the equation of the right line MN.

By eliminating x^2_3 out of the equations (k_4) and (1), we find

$$x_1 = 0, \; x^2_2 = 0. \text{ and } MN \equiv (n - \mu m)^2\,x_1 + \mu\,(a^2x_2 - bx_3) = 0 \quad (2)$$

so all these lines MN, passing through the point R, determine a pencil $[R]$. We put

$$\frac{\mu}{(n-\mu m)^2} = \varrho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and from this ensues the equation

$$m^2\varrho \, . \, \mu^2 - (2\varrho mn + 1)\,\mu + n^2\varrho = 0,$$

giving the correspondence between ϱ and μ. Each value for ϱ furnishes *two* values for μ, and for each value of μ we find *one* value for ϱ.

The curve k_4 can therefore be determined *by means of an involutory pencil of conics* (1) *and a projective pencil of rays* (2). It is easy to see, that these two pencils have $x_1 = 0$ as a corresponding common element and that consequently the generated curve of order five breaks up into $x_1 = 0$ and the curve k_4. All those conics of the pencil (1) have two tangents $x_1 = 0$, $x_2 = 0$ in common, and the vertex (R) of the pencil of rays is situated on the first of these tangents.

3. The points of contact D_1 and D_2 on the double tangent d, are projected out of the cusp A by two right lines, the equation of which will be obtained by eliminating x_1 out of (k_4) and (d); so from

$$[4m^2x_3^{\,2} + x_2\,(a^2x_2 - bx_3)]^2 - 16m^2x_2x_3\,(a^2x_2 - bx_3) = 0$$

we find

$$AD_1\,,\,AD_2 \equiv 4m^2x_3^{\,2} - x_2\,(a^2x_2 - bx_3) = 0.$$

By eliminating $x_2\,(a^2x_2 - bx_3)$ out of the latter equation and (k_4), we have

$$(mx_3^{\,2} + nx_1x_2)^2 - 4m^2x_3^{\,4} = 0$$

or

$$mx_3^{\,2} + nx_1x_2 \pm 2mx_3^{\,2} = 0,$$

therefore

$$nx_1x_2 - mx_3^{\,2} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$nx_1x_2 + 3mx_3^{\,2} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

On these conics lie the points of intersection of k_4 with the pair of lines $AD_1\,,AD_2$. The first conic (4) gives by combination with the equation (k_4) again the double tangent (d), and the second conic (5) furnishes by eliminating $x_3^{\,2}$ out of (k_4) and (5) the equation

$$3m\,(2nx_1x_2)^2 + 9nx_1x_2^{\,2}\,(a^2x_2 - bx_3) = 0$$

or

$$4mnx_1 + 3\,(a^2x_2 - bx_3) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

On this line lie the two points $D'_1\,,\,D_2$ of intersection of k_4 with the projecting rays $AD_1\,,AD_2$.

The line $D'_1D'_2$ cuts the curve k_4 again in two other points $E_1\,,E_2$ and bears four projecting rays out of the cusp A. This quadruple of rays will be obtained by eliminating x_1 out of (6) and (k_4), namely

$$16m^4x_3^4 - 40m^2x_2x_3^2(a^2x_2 - bx_3) + 9x_2^2(a^2x_2 - bx_3)^2 = 0,$$

and consequently the expression to the left must be divisible by the left side of the equation for AD_1, AD_2, i. e. by

$$4m^2x_3^2 - x_2(a^2x_2 - bx_3).$$

The division gives the equation of the pair

$$AE_1, AE_2 \equiv 4m^2x_3^2 - 9x_2(a^2x_2 - bx_3) = 0.$$

By eliminating $x_2(a^2x_2 - bx_3)$ out of the latter equation and (k_4), we obtain

$$(mx_3^2 + nx_1x_2)^2 - 4m^2x_3^4 = 0,$$

therefore

$$3nx_1x_2 + mx_3^2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$3nx_1x_2 + 5mx_3^2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

On the conic (7) are situated the points E_1, E_2, and on the conic 8) the points E'_1, E'_2 as the fourth intersections of k_4 with the pair of lines AE_1, AE_2.

The equation of $E'_1E'_2$ will be acquired by combination of (8) with (k_4); if we eliminate x_3^2, we obtain:

$$E'_1E'_2 \equiv 4mnx_1 + 15(a^2x_2 - bx_3) = 0 \quad . \quad . \quad . \quad . \quad (9)$$

In pursuing these projections in this manner we can show that the general equation of all these lines $D'_1D'_2$, $E'_1E'_2$, $F'_1F'_2$, and so on, will be

$$4mnx_1 + [(2k)^2 - 1](a^2x_2 - bx_3) = 0 \quad . \quad . \quad . \quad . \quad (10)$$

k being any entire positive number or zero. All these projections are also elements of the pencil $[R]$.

The parameters in the equation (10) belonging to the mentioned projections are of the form

$$\varrho_i = \frac{(2k)^2 - 1}{4mn}, \; (i = k = 0, 1, 2, 3, \ldots\ldots).$$

We conclude from this that

the cross ratio of any four projections, determined by the equation of the form (10) *is independent of the coefficients in the equation of k_4, or, this cross ratio for the same four values of k is unaltered for all curves of the considered form.*

The double tangent d, having the equation

$$4\,mnx_1 - (a^2x_2 - bx_3) = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (d)$$

belongs also to the projections (10); indeed, the equation (10) furnishes the equation (d) for $k = 0$.

Retaining the three lines

$$x_1 = 0$$

$$a^2x_2 - bx_3 = 0$$

and

$$4\,mnx_1 - (a^2x_2 - bx_3) = 0,$$

we can change the fourth ray, the equation of which is of the form (10). The cross ratio of these four lines will be:

$$\triangle = 1 - (2k)^2 \qquad (k = 1, 2, 3, 4, \ldots\ldots).$$

therefore the value of $\triangle$ *is independent of the curve* k_4, *and is a function of* k *alone.*

4. We have seen, that in the projective generation of k_4 to any ray of pencil $[R]$ correspond two conics of the involutory pencil. The values of the parameters μ for these conics, which correspond to the right lines, indicated by (10), will be determined out of the equation, with respect to (3):

$$\frac{(2k)^2-1}{4mn} = \frac{\mu}{(n-m\mu)^2}$$

This quadratic equation furnishes two pairs of values for μ, namely

$$\mu_{1,2} = \frac{n\,[2k \pm 1]}{m\,[2k \mp 1]}.$$

We can now determine any number of discrete points of k_4 as follows; putting

$$p \equiv a^2x_2 - bx_3 = 0$$

we can write

$$\left.\begin{array}{r} 4\,mnx_1 + [2k+1]\,[2k-1]\,p = 0 \\ m\,[2k \mp 1]\,x_3^2 + n\,[2k \pm 1]\,x_1x_2 = 0 \end{array}\right\} \quad (k = 0, 1, 2, 3, \ldots\ldots),$$

m, n being whatever constant numbers and p any right line passing through A 1). If we eliminate x_1 out of the equations of the latter system, we shall obtain two pairs of pencils with non-consecutive rays in a correspondence (1, 2) i. e. $[R]$, $[A]$, having the equations

$$\left.\begin{array}{r} 4\,mnx_1 + [2k+1]\,[2k-1]\,p = 0 \\ 4\,m^2x_3^2 - [2k \pm 1]^2\,px_2 = 0 \end{array}\right\} (k = 0\ 1, 2, 3, \ldots\ldots),$$

where the coefficients have an interesting form.

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1) In my paper: *Ein Satz über die ebene Kurve 4. Ordnung mit einer Spitze 2. Art*, Sitzungsberichte der K. Akademie in Wien, IIa, CXIX, 1910, I have considered a few similar relations for this curve of deficiency *one*. Next time I shall treat the same relations for a quartic curve with a spinode and a rhamphoid cusp (deficiency zero).

5. The line $RB \equiv x_1 = 0$ cuts k_4 still in two points P_1, P_2; projecting these points out of the cusp A, we obtain two lines having as equation

$$m^2 x_3^2 - x_2 (a^2 x_2 - b x_3) = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Eliminating $x_2 (a^2 x_2 - b x_3)$ or $x_2 \cdot p$ out of k_4 and the latter equation, we have

$$(m x_3^2 + n x_1 x_2) \pm m x_3^2 = 0$$

therefore

$$x_1 = 0 \quad , \quad x_2 = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

$$2 m x_3^2 + n x_1 x_2 = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

The equation (b) defines a conic, passing through the two points $P'_1 P'_2$ in which the curve k_4 is cut still by the pair of lines (11). By eliminating x_3^2 out of (k_4) and (b) we obtain the equation of $P'_1 P'_2$ in the form:

$$P'_1 P'_2 \qquad m n x_1 + 2p = 0.$$

On the line $P''_1 P''_2$ lie two other points Q_1, Q_2 common to k_4 and $P''_1 P''_2$; so we can now project the points Q_1, Q_2 out of A by two lines cutting k_4 still in the fourth intersections Q'_1, Q'_2, and so on.

There is no difficulty to show, that the general equation of all these projections $P'_1 P'_2$, $Q'_1 Q'_2$, $S'_1 S'_2$, ... , will be

$$m n x_1 + k(k + 1) p = 0 \quad , \quad (k = 0, 1, 2\ 3, \ldots), \quad . \quad . \quad (12)$$

and we see, that all these projections are again elements of the pencil $[R]$.

By means of the involutory pencil of conics (1) we find with respect to (3) and (12):

$$\frac{k(k+1)}{mn} = \frac{\mu}{(n - m\mu)^2}.$$

From this equation follows:

$$\mu_1 = \frac{n(k+1)}{mk} \quad , \quad \mu_2 = \frac{nk}{m(k+1)},$$

therefore any line having the form (12) cuts k_4 on the two conics:

$$\left.\begin{array}{r} m k x_3^2 + n(k + 1) x_1 x_2 = 0 \\ m(k + 1) x_3^2 + n k \; x_1 x_2 = 0 \end{array}\right\} \quad (k = 0, 1, 2, 3, . \; .) \quad . \quad (13)$$

By eliminating x_1 out of (12) and (13) we obtain two pairs of pencils with non-consecutive rays in correspondence (1, 2), by means of which any number of discrete points of k_4 can be determined; thus

$$\left.\begin{array}{r} mnx_1 + k(k+1)p = 0 \\ m^2x_3^2 - (k+1)^2 x_2 p = 0 \\ m^2x_2^2 - k^2 x_2 p = 0 \end{array}\right\}\Bigg\{ ,$$

k being any entire positive number or zero.

Let us observe, that any four lines having an equation of the form (12), give a cross ratio which is independent of the coefficients in the equation of k_4, or, what is the same, that the *cross ratio* for the same four values of $k = 0, 1, 2, 3, \ldots\ldots$ is *unaltered for all the curves of the considered form.*

If we retain the three fixed rays

$$x_1 = 0 \quad , \quad p = 0,$$
$$4\,mnx_1 - p = 0,$$

any line of the form (12) gives with these three rays an absolute constant cross ratio for all the curves of the species k_4, where k is a constant number:

$$\angle' = -\frac{1}{4k(k+1)},$$

also *a function of the chosen value of k for the same curve k_4.*

6. We have already indicated the two systems of projections, the *first* of which is acquired by projecting the two points of contact on the double tangent out of the cusp A, and the *second* by projecting the two common points to k_4 and $x_1 = 0$ out of the same centre of projection. We take now two of those projections, belonging to *various systems* for the same value of k, having the equations

$$4mnx_1 + [(2k)^2 - 1]\,p = 0$$
$$mnx_1 + k(k+1)\,p = 0.$$

By the term "same value of k" for the two systems is meant that the *same number of projections* was made in both systems. These rays of the pencil $[R]$ bear with the fixed pair of rays

$$4mnx_1 - p = 0 \quad \ldots\ldots\ldots \quad (d)$$
$$p = 0$$

a cross ratio $\angle''$. By means of the parameters

$$\frac{mn}{k(k+1)}, \quad \frac{4mn}{(2k)^2-1}, \quad 0, \quad -4mn,$$

we shall obtain

$$\angle'' = \left(\frac{2k}{2k+1}\right)^2, \quad (k = 0, 1, 2, 3, \ldots.),$$

therefore *a value invariable for all the curves k_4 with a rhamphoid cusp and a node,* if the *same* value of k for all such curves has been chosen.

We see yet also, that the four points of intersection of the curve k_4 with each line h, passing through R, this point R, and the common point to h and $x_2 = 0$ are three pairs of *the same involution.* Then the pair $x_1 = 0$, $x_2 = 0$ is a degenerated conic of the pencil of conics (1) which bears k_4 with the projective pencil $[R]$.

7. A line passing through the point (M) of intersection of the double tangent (d) and the cuspidal tangent ($x_2 = 0$) has an equation of the form

$$\mu^2 x_2 + (4mnx_1 - a^2x_2 + bx_3) = 0 \quad . \quad . \quad . \quad . \quad . \quad (14)$$

If we eliminate d out of (14) and (k_4), writing the equation of k_4 in the form

$$(mx_3^2 - nx_1x_2)^2 + x_2x_3^2\,(4mnx_1 - a^2x_2 + bx_3) = 0 \quad . \quad . \quad . \quad (k_4)$$

we shall obtain

$$\mu^2 x_2^2 x_3^2 - (mx_3^2 - nx_1x_2)^2 = 0$$

therefore

$$\mu x_2x_3 \pm (mx_3^2 - nx_1x_2) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

To any ray of the pencil $[M]$ corresponds a pair of conics (15), which form an involutory system for all values of μ. The two conics of the conjugate pair have in the vertex B a pair of tangents

$$\mu x_3 \pm nx_1 = 0,$$

which is divided harmonically by the two lines $x_1 = 0$, $x_3 = 0$. All the conics of the involutory system osculate one another in the cusp A on $x_2 = 0$.

From this follows an other generation of k_4.

> *Let be given an involutory pencil of conics, which osculate each other in a point (A) on the common tangent ($x_2 = 0$), and a pencil of rays $[M]$ having its vertex (M) on the tangent $x_2 = 0$, then we can arrange a correspondence between these pencils in this manner, that the parameter of a ray in the pencil $[M]$ is the square of the parameter belonging to the corresponding conjugate pair of conics in the involutory pencil.*

The two pencils generate a curve of order five, which breaks up into the common corresponding right line $x_2 = 0$ and the curve k_4 of the considered species.

If we choose under all these conjugate pairs of conics that, for which the two tangents in the point B are identical with the tangents

$$nx_1 \pm ax_3 = 0$$

of the curve k_4 in the same point, then this pair will meet k_4 in two points U_1, U_2; we obtain the joining line of these points out of the equation of the considered pair of conics, i. e. out of

$$ax_2x_3 \pm (mx_3^2 - nx_1x_2) = 0;$$

so we have by the latter definition

$$U_1U_2 \equiv a^2x_2 + d = 0$$

or

$$U_1U_2 \equiv 4\,mnx_1 + bx_3 = 0,$$

and this is the line passing through the vertex B and the common point (M) to the double tangent and the cuspidal tangent. Therefore the four points U_1, U_2, B, and M lie on a straight line.

On each line passing through M we have obtained four points of k_4 as intersections of this line with two conics belonging to a pencil, which has three consecutive base-points in A, and the fourth base-point in B. To this pencil of conics belongs also the pair of lines $x_3 = 0$, $x_2 = 0$ as a degenerated conic. We can now say, that on each line s, passing through M, the two pairs of intersections with k_4, the point M and the common point to s and $x_3 = 0$ are *three pairs of elements of the same involution.*

All the relations considered here, remain unaltered, if the double point B is a "conjugate point" (acnode).

Anatomy. — "*On the development of the Hypophysis of Primates especially of Tarsius*". By Prof. L. Bolk.

(Communicated in the Meeting of November 26, 1910).

When studying an Embryo of Tarsius spectrum belonging to the embryological Institute of the Utrecht University (Catalogued as Tarsius n° 666), my attention was drawn by the peculiar shape of the pharyngeal part of the Hypophysis. In this Primate a form is developed more complicated than is known to us in other mammals. In most cases we know, as follows from the description of various authors, that the Hypophysis-vesicle unstrings itself from the roof-epithelium of the stomadeum, places itself against the anterior surface of the infundibularstem, and is then, when the nervous part of the Hypophysis begins to develop, invaginated by the latter. The pharyngeal — or more correctly expressed — the oral part of the Hypophysis consequently becomes a vesicle with double parietes in the invaginated cavity of which the cerebral part of this organ is received.

There was sufficient reason to accept, likewise for Tarsius, this very simple mode of development, as **Ziehen**, who has made a special study of the development of the brain of this primate, with specimens likewise belonging to the Utrecht university, does not speak of any deviating form of development, but points emphatically to a conformity with the usual course of development. So he says e. g. on page 351 of the second volume, third part of **Hertwig**'s Handbuch der Vergl. u. Experimentellen Entwicklungsgeschichte der Wirbeltiere: "Die charakteristische Umklammerung des Hirnteils der Hypophyse durch den Rachenteil giebt die nachstehende Figur wieder." In his communication, published in the reports of this Academy [1]) he holds the same view.

My observation with regard to Tarsius suggested to me the idea of studying the first origin and the formation of the Hypophysis vesicle likewise in the other embryological specimens of Primates that were in my possession. And the result of this study was that at least one of the peculiarities I found in Tarsius, was elucidated. For it appeared to me, that the way in which the Hypophysis of Primates originates and develops itself corresponds almost entirely to that of Reptiles. An exact description of it we owe to **Gaupp**. With this group of vertebrates the vesicle does not originate in a single but in a triple invagination, a median and two lateral ones. Whereas the median invagination more specially joins the nervous part of the Hypophysis, the parts distinguished by **Gaupp** as lobuli laterales develop from the lateral invaginations [2]). It is exactly so with Primates. Here also what **Gaupp** calls the "Vorraum" develops itself first, and behind it follow the three invaginations lying beside each other.

In Figure 1*a*—*f* are represented, as a proof of this fact, a few sections through the origin of the Hypophysis of a young embryo of Macacus cynomolgus (Embr. Mus. Utrecht Selenka's Material Embryo "Grethe". The direction of the section was a little slanting. In *a* the "Vorraum" has been struck, in *b* the invagination of one of the lobuli laterales is to be seen, in *d* the median part has placed itself against the infundibular-stem, and the unstringing begins, which is completed in *e* and *f*. I shall not enter into further details of these facts. I only mentioned them to comprehend more easily the form of the Hypophysis of Tarsius. Only this be added to the above, that

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[1]) These Proc. of 26 Nov. 1904.

[2]) **Staderini** afterwards observed these lobes likewise in larvae of Triton cristatus.

with Primates the glandular differentiation of the organ is limited to the lobuli laterales, and to the "Vorraum", whilst the median invagination constitutes only a covering parietes round the nervous part.

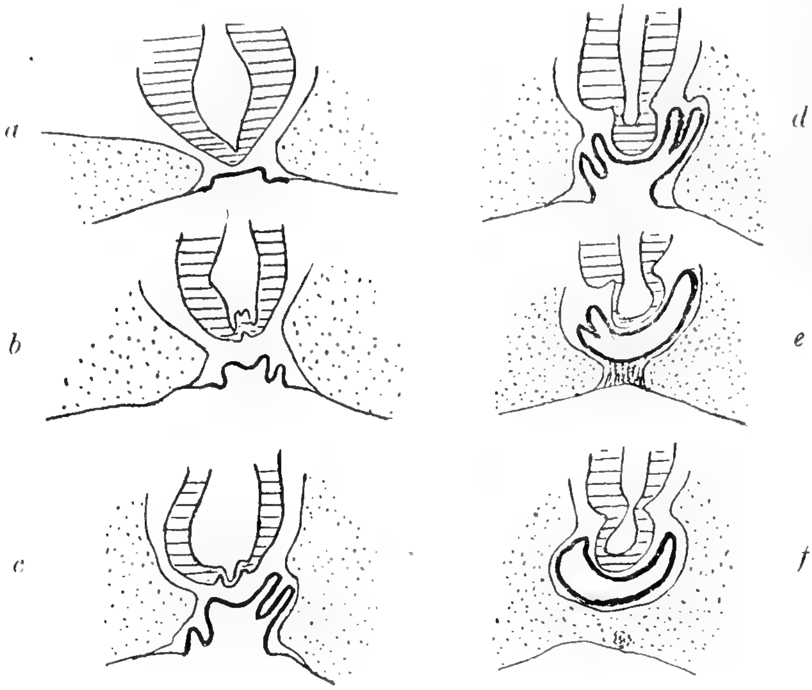

Fig. 1.

Let us now return to Tarsius. I have reconstructed a model a hundred times enlarged of the Hypophysis of the above mentioned Embryo N°. 666 corresponding in its development to N°. 34 of KEIBEL's Normentafel. This model is represented in fig. 2 as seen from aside. The lines running vertically through this figure indicate the direction of the section, and the sections indicated by these lines are sketched in the figures 3*a*—*i*.

In the first place it is conspicuous in this figure that the pharyngeal part of the Hypophysis consists of two parts, a larger, the real vesicle, into which from behind the nervous part (indicated by a thicker line) is invaginated, and a narrower one apparently turned down between the basis of the brain and the larger part in the direction of the infundibular-stem. As this part bifurcates in the shape of a two-pronged fork, I shall indicate it as Lobulus bifurcatus.

As appears from figure 2 this lobe is connected at the forepole of the Hypophysis with the other part. In this anterior part the formation of cell-strings has begun. This is the reason that the surface shows here irregular outward protuberances. These are still continued at the very beginning of the Lobulus bifurcatus. The section corresponding to the line *a* in figure 2 is sketched in figure 3*a*. One sees that at one side (in the figure to the right) the Lobulus bifurcatus is already separated from the rest of the mass

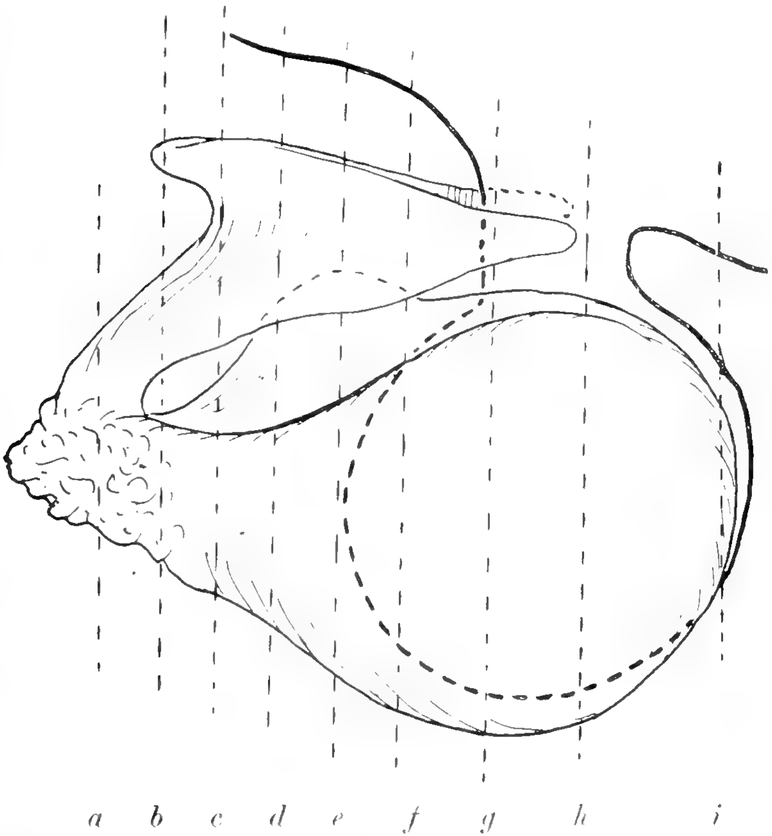

Fig. 2.

More backward this lobe assumes in the section the shape of a little hood, the two sides of which meet under an obtuse angle. The parietes become flat (figure 3*b*) and whilst the connection between the two halves in the median-line becomes broader, an offshoot is formed from the foremost edge in a frontal direction. In order to understand this, one should compare the section figure 3*b* with the level indicated in figure 2 by line *b*. We see that this line passes successively through this offshoot, the stem of the Lobulus bifurcatus and the foremost part of the Hypophysis vesicle. No lumen however is to be seen in any of these sections.

Afterwards a combshaped protuberance develops itself from the concave superior plane of the vesicle, penetrating into the concavity of the Lobulus bifurcatus (figure 3*c*). In connection with this the last

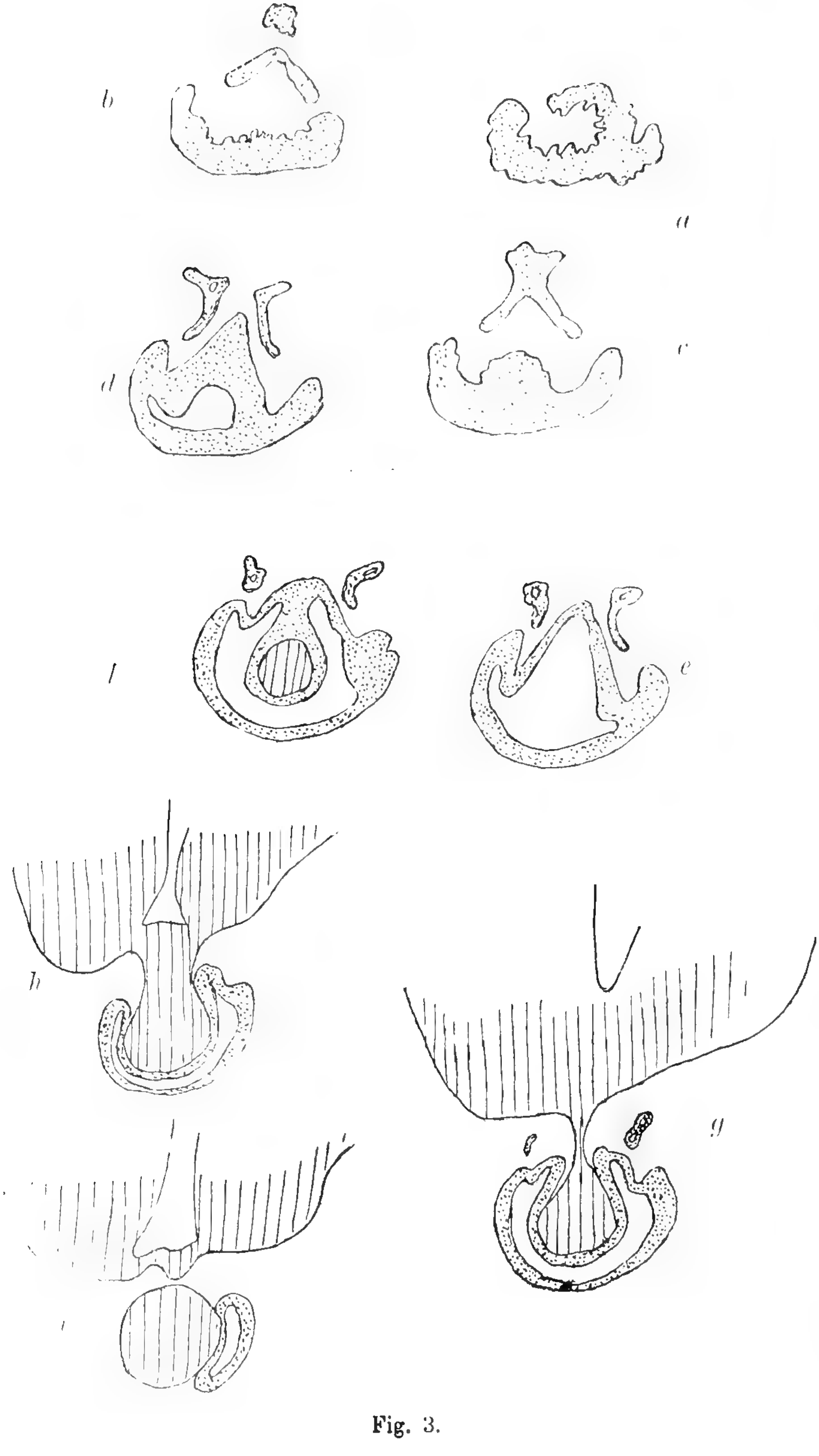

Fig. 3.

mentioned lobe divides into a right and a left half, and as soon as this division has taken place (figure 3*d*) a lumen appears in both halves. These two halves might be designated as the horns or cornua of the Lobulus bifurcatus. In section they are hook shaped, the outside plane is, especially in the foremost part, very concave. Both horns become more pointed towards the hind-parts, preserve however their lumen nearly to their extremities. These ends lie on either side of the infundibularstem (figure 3*g*). Into the hindmost part of the Hypophysis vesicle the nervous part is invaginated. This pars nervosa is not completely surrounded by the pharyngeal one, the part that is turned to the back remains free.

If we contemplate the shape of this vesicle more carefully, we can clearly distinguish a central part and two lateral parts. Especially in the foremost half, where the comb-shaped protuberance of the central part begins, these lateral parts are very distinct. As appears likewise from Figure 2, they can be followed as far as the hindmost part of the vesicle. From what I know about the first origin of the Hypophysis vesicle of other Primates I do not feel the least doubt that these lateral parts are the lobuli laterales, described by GAUPP with the Reptiles. I repeat that it is in these lateral lobes that, with Primates, the ensuing histological differentiation of the Hypophysis vesicle is continued. They form consequently an essential ingredient part of the Hypophysis.

I shall not venture to express a view of the signification of the lobulus bifurcatus. Certain it is that the two cornua do not play an important part in the further development. This appears from the condition found in an older Embryo (Embryol. Laborat. Utrecht Tarsius N°. 555). Three sections through the Hypophysis of this specimen are represented in Figure 4. Section *a* in this figure is nearly similar to Figure 3*b*. One recognises the foremost part of the vesicle, differentiated to cell-stems, but the part of the Lobulus bifurcatus (ridge-shaped in the section) lying above it shows also a similar course of development. On the top of it lies the section of the beginning of the cornua, each provided with a lumen. The fact that the latter likewise still show progressive symptoms of development, appears from Figure 4*b*, where on either side of the infundibular-stem groups of cells are found, among which there are some with a lumen, which have taken their origin in the cornua. And that such epithelium-isles extend as far as the hindmost edge of the infundibular-stem appears from Figure 4*c* in which a section is sketched, lying behind the above-mentioned stem, and where after all, at least on one side, remains of the Lobulus bifurcatus are found.

Especially from the location of these latter remains appears a topographical peculiarity of the Lobulus bifurcatus of Tarsius which

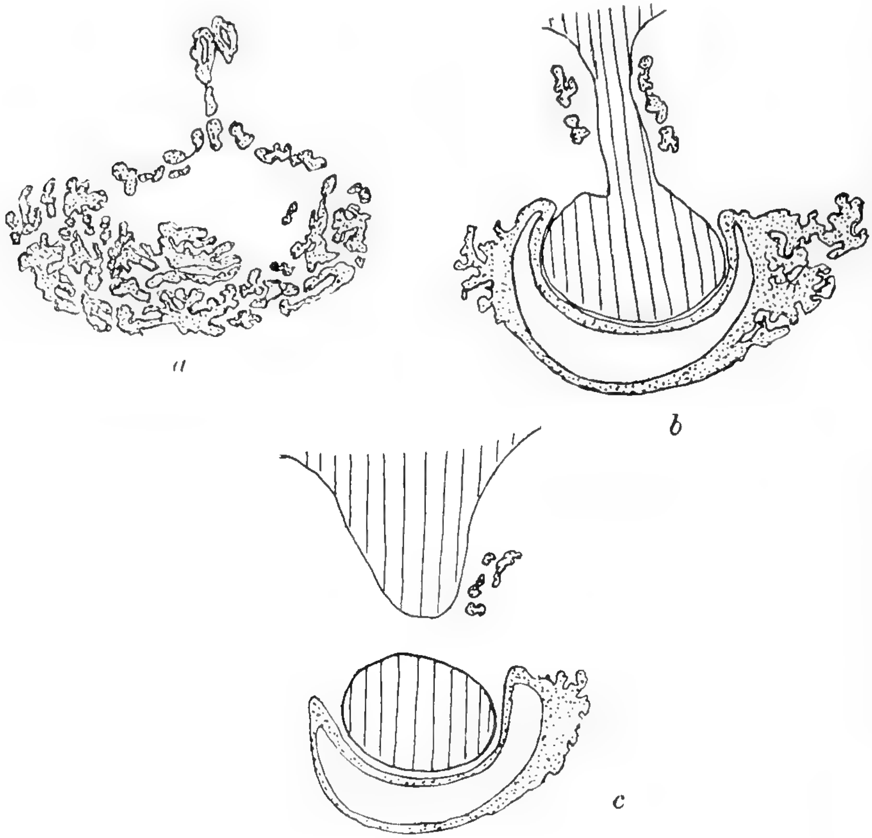

Fig 4.

perhaps is not unimportant for its significance. It is clear in fact that these parts of the pharyngeal Hypophysis are not lying in the sella turcica. They lie in the subarachnoideal sinus directly against the basalplane of the brain, above the diaphragma sellae formed by the Dura mater.

Finally I draw the attention to the fact that from Figure 4^b it appears that it is chiefly the lateral parts of the Hypophysis vesicle that constitute the principal part of the pars glandularis of the fullgrown Hypophysis. The centralpart remains — at least with Primates — more indifferent.

The study of the earlier periods of development of the Hypophysis vesicle of younger embryos of Tarsius than I had to dispose of for the moment, is certainly to be recommended, especially with a view to the way in which the Lobulus Bifurcatus originates.

Microbiology. — *"Fat-splitting by bacteria."* By Dr. N. L. SÖHNGEN. (Communicated by Prof. Dr. M. W. BEIJERINCK).

(Communicated in the meeting of November 26, 1910).

Our knowledge about fat-splitting by bacteria, a process interesting as well for its practical value for several industries, as for scientific reasons, must hitherto be considered as very deficient when compared with what we know of the breaking off of carbohydrates and proteids.

This relatively little knowledge should be ascribed to various causes.

In the first place there is no urgent motive to study fat-splitting by organisms for technical purposes, in as much as technical fat-splitting is without much trouble effected chemically or enzymatically. Moreover, in the splitting of fat do not result such striking conversion products as in the breaking off of carbohydrates and proteids by bacteria, so that this process may easily be overlooked by the experimenter.

To this we may add that the decomposition of fat proceeds in general slowly, so that a prolonged cultivation is required before a sufficient quantity of material is formed for making the analyses, which, besides, are by no means simple.

Fat-splitting by microbes is notwithstanding of great signification for the industry of fats by the highly prejudicial consequences accompanying this process.

So we should not be astonished that the greater number of investigations in this line have been made especially in behalf of the dairy industry; so that rancidity of butter and fat-splitting in cheese have best been studied.

1. HISTORICAL.

We shall only give a short survey of those investigations on fat-splitting which have been made in recent times.

REINMANN [1]) stated in 1900 that the rancidity of fats must not be ascribed to the influence of air as was then the common opinion. The action of microbes he did not mention. The growing tallowy of fats was after REINMANN caused by the action of light in presence of air.

JENSEN [2]) attributes rancidity wholly to microbic action. Of the

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[1]) Centralblatt f. Bakt. 2 Abt. 1202. Bd. 6 S. 166.

[2]) Landw. Jahrb. d. Schweiz 1901. Bd. 15 S. 329.

organisms isolated from rancid butter *Oidium lactis*, *Cladosporium butyri*, *Penicillium glaucum* and *Streptotrix alba* proved vigorously to split fats, whilst *B. fluorescens liquefaciens*, *B. prodigiosum* and *B. mesentericus vulgatus* belong to the feebler splitters. According to JENSEN part of the fat in cheese is also splitted, especially at the outside.

The researches of LAXA[1]) with pure cultures of fat-splitting organisms inoculated into sterilised casein, made of unskimmed milk, showed that *B. fluorescens liquefaciens*, *Oidium lactis*, *Penicillium glaucum* and a *Mucor* species split butter.

KÖNIG, SPIECKERMANN and BREMER[2]) published researches on the decrease of fat percentage in cattle-cake by microbic action. According to them this percentage may be reduced from 10%—12% to a few per cents within the time of a year.

HUSS[3]) isolated from milk a *Bacterium lipolyticum* which in milk and butter causes a rancid, bitter taste. The description of this bacterium we briefly give as follows.

Bacterium lipolyticum is a coccus-shaped, 0.3—0.5 μ wide, and 0.7—1.4 μ long motile rod; liquefies gelatin slowly without film formation, coagulates milk at 20° C. in three days, then dissolves the casein; the culture is then dirty yellow, has a putrid smell and reacts alkaline. Indol is produced in slight quantity; methylene blue is reduced, nitrate is reduced to nitrite, lipase is secreted. Acid production occurs from glycerin, mannite, dextrose, saccharose, raffinose and xylose, not from lactose.

From a sample of quickly creaming milk WOLFF[4]) isolated a bacterium, the cause of this phenomenon. The shape of this microbe is like that of *B. lactis acidi*: size of the cells 0.6—0.8 μ × 1—1.5 μ. Slightly motile. On gelatin this bacterium grows out to small colonies having the form of a flower-head of *Bellis perennis*. Gelatin and casein are not liquefied. In milk this microbe grows well and forms a film; the reaction of the liquid is alkaline and it smells like soap.

Besides in the dairy industry, researches on fat-splitting in the soil have been made. In 1900 RUBNER[5]) published a treatise on this subject in which the splitting and assimilation of fat by microbes in the soil is stated. This experimenter found that in a year ± 50% of the fat added to the soil was split and ± 15% assimilated. A vigorous splitting of the additional fat also occurs in culture liquids, especially

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[1]) Archiv. f. Hyg. Bd. 41 1902.

[2]) Zeitschr. f. Unters. der Nahrungs- und Genussmittel 1901 Heft 16 S. 720.

[3]) Centralblatt f. Bakt. 2 Abt. 1908 Bd. 20 S. 474.

[4]) Milchwirtsch. Zentralbl. 1909 p. 500.

[5]) Arch. f. Hyg. 1900 Bd. 38 S. 67.

in those containing an easily assimilable source of nitrogen, such as peptone or proteids, after inoculation with garden soil. Addition of calcium nitrate to this culture medium proved very favourable for the process.

In his experiments with the pure culture of a fat-splitting bacterium in broth, calcium nitrate and 4.424 grs. of fat, after 35 days' cultivation at room temperature, more than the half was split and ± 0.7 gr. assimilated; after a cultivation of more than a year, however, nearly all the added fat was split, more than the half being assimilated.

The fatty acids and the glycerin formed from the fats are oxydised without intermediate products to carbonic acid and water.

BECHHOLD[1]) demonstrated that fats and soaps disappear in the sewage mud of the installations for the purification of water at Stettin, by bacterial action.

EYKMAN[2]) gives in a treatise on fat-splitting bacteria, beside other facts, a simple and nice method to demonstrate lipase secreted by micro-organisms. This method is based on the splitting action of diffusing lipase, produced by bacterial streaks on agar or gelatin, on a thin fat layer at the underside of this substratum. The fat, decomposed under the bacterial mass has the appearance of an opaque white stripe, very distinct from the non-decomposed fat.

According to EYKMAN the following bacteria split fat: *B. pyocyaneum*, *Staphylococcus pyogenes aureus*, *B. prodigiosum*, *B. indicum*, *B. ruber*, *B. fluorescens liquefaciens*.

RAHN[3]) has studied fat-splitting by microbes on a culture medium of the following composition. In an inclined ERLENMEYER flask some fat is melted. After cooling the flask is put upright and a thin layer of an anorganic culture liquid is filled into it.

After inoculation with garden soil a good growth of moulds and bacteria results, which, after transference to a similar flask soon recommences.

Four fat-splitting moulds and two fat-splitting bacteria were isolated on culture plates of an anorganic nutrient liquid solidified with agar and containing tributyrin in finely divided state. On these plates a clear field appears around the colonies of fat-splitting microbes, in consequence of the splitting action of the diffusing lipase on the tributyrin, and of the solution of the products formed in the medium.

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[1]) Zeitschr. f. Angew. Chem. 1898 S. 849 cit. [4]).

[2]) Eighth Dutch Phys. and Med. congress 1901 p. 171.

[3]) Centralblatt f. Bakt. 2 Abt 1906 Bd. 15 S. 422.

De Kruyff[1]) has made a research at Buitenzorg on fat-splitting bacteria in the tropics. For the isolation of the microbes he first accumulated them in Erlenmeyer flasks provided with a thin layer of an anorganic culture liquid and finely divided fat. The inoculation was made with soil, water, or excrements; cultivation at 37° C. Transplantation to a same culture liquid produces an exclusive growth of fat-splitting organisms.

Nine fat-splitting species were isolated, all *Lipobacter*-species. Of these four are fluorescents, two correspond in many respects to the *Bacterium pneumoniae*, whilst *Lipobacter* N°. 4 is a yellow non-liquefying micrococcus.

Quantitative determinations show that by some species in 12 days all the fat is split and one half oxydised. In a paper on thermophilous bacteria de Kruyff[2]) mentions that also among these sporulating species some are found which secrete lipase,

II. Proof of the fat-splitting power of micro-organisms. Lipase.

In two ways the fat-splitting power of micro-organisms may be stated: 1. by means of titration of the fatty acids split off by an organism from the fat; 2. by properly rendering visible the produced fatty acids and soaps.

The first method may be successfully applied in the investigation of preparations in which concentrated lipase occurs. It will always be necessary to apply it for quantitative determinations of fat-splitting. The second way, including the methods followed by Rahn, de Kruyff, and Eykman, should be preferred for qualitative determinations on account of its great sensitiveness.

On the plates some of Eykman's culture plate reactions are represented. The white fields of Plate *A* are formed on the left by a *B. lipolyticum α*, described on page 674, and on the right by *B. Stutzeri*, both cultivated on broth agar. Plates *B* and *C*, on which *B. lipolyticum β* and *B. denitro fluorescens non-liquefaciens*, contain broth agar with additon of respectively 4 °/₀ glucose and 4 °/₀ glycerin. The peculiar fields of *D* are obtained by allowing the culture plate to lie for some weeks after the agar layer has been removed.

These figures show that glucose and glycerin exert little influence on the degree of decomposition by lipase; this becomes, however,

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[1]) Bull. du Départ. de l'Agric. aux Indes Néerland. 1907 cit. Centralblatt. f. Bakt. 2e Abt. Bd. XX S. 610.

[2]) Bull. du Départ. de l'Agric. aux Indes Néerland. 1909. N. XXX Microbiologie IV.

the case as soon as from those compounds acids are formed, as wil be shown below.

When considering attentively the decomposed portions of the culture plates we observe that around each white central part of a field, consisting of fatty acid, soap, and compounds of lipase with fatty acid, a less white band extends formed from fatty acids. Around this less white part another band is found characterised by still more clearness, it is even more transparent than the non-decomposed adjoining fat. This clear portion is formed in consequence of the disappearance of the fat-crystals, caused by the lipase action.

These bands are very well seen in the figure; on the culture plates themselves they can be distinguished still better.

The same is observed respecting little staves of fat placed in a lipase solution. Fig. 1, 2 and 3 Pl. 4 are drawings (24 times magnified) of pieces of dry fat kept for 30 days at 20° C. in test tubes of broth inoculated with fat-splitting microbes. On the outside of the fat (in the figure at the top) is a bacterial film under which a white saponaceous part (on the plate cross-hatched) then a layer consisting of fatty acids (hatched), and finally the non-decomposed fat.

The diffusion velocity of lipase in dry fat is, as the experiment shows, very small. In one month the lipase has penetrated into the fat not more than half a millimeter. In moist fat that velocity is much greater. The great difficulty however, evenly to emulsionate water and fat, makes comparative experiments as to the diffusion velocity of lipase in fat containing different quantities of water almost impossible.

As said above, the rate of acidity of the medium influences the degree of decomposition of fat by fat-splitting microbes. When using an acid culture agar for the lipase reaction after EYKMAN we see under and around the bacterial inoculation streaks in the fat layer a wide field appear, but we do not perceive a white central part as is the case when the plate is alkaline.

From a series of experiments which will be discussed in a separate communication, followed that for some micro-organisms two lipases are formed which, besides by their different diffusion velocity, are also characterised by their different behaviour towards acids.

Thus, *B. Stutzeri* and *B lipotyticum* secrete two lipases, *α-lipase* and *β-lipase;* the former diffuses more rapidly than the latter and splits fat as well in an acid as in an alkaline medium.

β-Lipase is formed in an acid medium, but does not decompose fat in it, it may however, become active again after neutralisation of the medium.

Fat-splitting moulds and yeasts can be accumulated in a feebly acid culture liquid, which, besides fat or fatty acids, contains only anorganic salts, with garden soil for inoculation material. They produce, together with *endo-lipase,* often also *α-* and *β-lipase.*

In my experiments the fat-splitting power of bacteria was usually demonstrated by means of a method with fatcoated testtubes, which is carried out as follows.

The inner side of a sterile test tube is coated with a thin layer of fat; now a nutrient liquid is introduced in which the bacterium to be examined on lipase grows well and this bacterium is inoculated into it. If now lipase is produced in the culture we see after two or three days that portion of the fat which touches the liquid grows white; this appears first and most obviously at the place where the bacterial growth is strongest. Aërobes decompose the fat first near the surface of the liquid, anaërobes first at the bottom of the tube.

On the accompanying photographs Pl. 3 we see a series of fatted tubes in which various fat-splitting microbes have decomposed the fat. In 1 no fat-splitting bacterium is inoculated, hence the fat has remained unchanged; 2 and 3 contain cultures with ammonium chloratum as source of carbon resp. of *B. Stutzeri* and *B. denitro-fluorescens non-liquefaciens*; 4 and 5 contain cultures of the same microbes but with kaliumnitrate as source of nitrogen; 6 contains a rough culture of a proteid putrefaction by inoculation with soil; 7 contains a rough culture of a pasteurised proteid putrefaction; 8, 9, 10, 11, and 12 contain cultures of various fat-splitting microbes isolated from soil and milk.

II. Fat-splitting microbes in the soil.

The microflora of the soil abounds in organisms which secrete lipolytic enzymes; a sowing of soil on a fatted plate after Eykman, or dilutions in fatted tubes show this most clearly. In one gram of humus we not seldom count some ten thousand fat-splitting ferments.

A. *Accumulations in culture media with ammonium chloratum as source of nitrogen.*

For the growth of bacteria, requiring beside fat as source of carbon only anorganic salts and ammonium chloratum as source of nitrogen, the following culture liquid was used.

100 tapwater
0,5 fat [1]) (finely divided)
0,5 calciumcarbonate
0,05 kaliumsulphate
0,1 magnesiumammonium-phosphate.

In this feebly alkaline medium the fat-splitting bacteria grow very well; the chalk and the magnesiumammonium-phosphate serve to neutralise the fatty acid and the acids resulting from glycerin.

Aërobic culture at 18°—25° *C.* If we inoculate a layer of the above medium, ± one centimeter thick, in an ERLENMEYER flask, with garden soil, sewage mud, canalwater or dung, and cultivate at 18°—25° C., a rapid increase of the bacteria introduced with the inoculation material ensues. After one or two transferences to a same medium there is an abundance of these microbes. The changes observed in the medium are the following: After one or two days the liquid becomes turbid by the bacterial growth and usually assumes a yellowish green colour; the floating pieces of fat sink down on saponification and subsequently change into slimy flakes.

Most of the bacteria present in the medium belong to the fat-splitting species; among them are melting and non-melting micrococci and fluorescents and species corresponding to *B. punctatum*. As well among the fluorescents as among the last named, stocks are found that split fat very vigorously, whereas others do this feebly or not at all.

If we take fatty acid instead of fat for source of carbon, the same flora occurs, whilst with glycerin very fine accumulations of *fluorescents* are obtained.

Aërobic culture at 30°—37° C. At these temperatures the culture presents quite another aspect as at those between 18°—25°. Thus we often find on the liquid a film of *Spirillum* especially when inoculating with sewage or canal water; it gets, however, lost after one or two transplantations. Evidently the spirilla have no lipolytic enzymes and grow at the expense of the products formed by other microbes. Sometimes a not inconsiderable growth of hay bacteria and butyric

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[1]) The fat used for these experiments is the so-called "suif pressé", a product remaining behind after pressing the oleo margarine from tallow. The melting-point is ± 55° C., the saponificationnumber 193—195. In consequence of the high melting point it is easy finely to distribate this fat in the culture liquid by shaking it in melted state with the latter and quickly cooling it. Also for culture at high temperatures (± 52°), for anaërobic culture and for experiments on denitrification with fats, it shows advantages over easily melting fats.

acid ferments takes rise in the medium inoculated with rough material; this neither reoccurs after transplantation.

After the first or second transplantation the flora chiefly consists of a group of aërobic bacteria of which four species have been isolated; *B. lipolyticum* α, β, γ, and δ. These bacteria have the shape of short double rodlets, 0.15 μ—1 μ wide and 0.25—2.5 μ long, slightly motile and wrapped in a slimy envelope. The colonies show resemblance to those of *B. aërogenes*; often the middle part is somewhat elevated. On broth gelatin after 5 days' culture at 20° C. they grow out to white or greyish white, sometimes slimy colonies, which after 5 days get a diameter of 1.5—2 mm. On broth agar they are more transparent and flatter.

The growth optimum is ± 35° C. They cannot resist heating for 10 minutes at 60° They thrive better on broth gelatin or broth agar than on media with salts of organic acids (malic acid and lactic acid) as carbon source and ammonium chloratum as source of nitrogen. On slices of potato these microbes grow out to white or greyish white moist colonies. Broth becomes very turbid after inoculation, at the bottom of the test tube a sediment forms, no film at the surface.

They thrive very well in milk which becomes viscous, alkali being formed. *B. lipolyticum* γ and δ form chymosine, the two others not or very little. Trypsine is not produced, neither diastase nor ureasa. Indican or aesculine are not split. On whey gelatine the growth is good and alkali is formed whereby an iridescent film appears. Indol is not produced, nitrate not reduced to nitrite, glucose is not fermented. The optimum of the lipase action lies near ±65°. In culture liquids containing ammonium chloratum as source of nitrogen a good growth is obtained with the following carbon sources: alcohol, glycerin, glucose, saccharose calciummalate, -lactate, -stearinate, aethylacetate, aethylbutyrate, tributyrine, trioleïne.

In a culture medium of the composition: 100 tapwater, 1 fat, 0,05 NH_4Cl, 0,05 K_2HPO_4, 1 $CaCO_3$, after ten days' cultivation at 25° *B. lipolyticum* α and β had split respectively 130 and 105 mGs. of fat, and assimilated 20 and 21 mGs. In brothwater, 2 °/₀ peptone, 1 °/₀ $CaCO_3$, and 1 °/₀ fat, in ten days respectively 630 and 480 mGs. of fat were split, and resp. 40 and 80 mGs. were assimilated.

Aërobic cultivation at 45°—55°. At these temperatures fat-splitting is seldom observed even with addition of large quantities of inoculation material (5 Gr.) to the medium. The cultures in which fat-splitting occurs contain a species closely allied to *B. mesentericus* nearly in pure culture; this species stands no transplantation to the same medium; after sowing out on broth agar with 2 °/₀ glucose, white or greyish white colonies result of 2—6 μ long rodlets, 1 μ wide. The spores resist boiling heat, gelatin is liquefied, diastase and lipase are secreted.

In a medium with mineral salts to which glucose, saccharose, glycerin, calciumlactate or amylum have been added, a good growth results after inoculation. Addition of peptone as source of nitrogen gives much stronger growth than ammonium chloratum. Stearinacid salts are not assimilated. The culture on slices of potato reminds of that of *B. mesentericus* on this medium, but the colour of the colony is whiter.

This microbe belongs to the group of hay bacteria and is distinguished by its lipase production; *B. mesentericus, B. subtilis* and *B. megaterium* isolated from potatoes do not secrete lipase.

Anaërobic culture. Under anaërobic conditions no growth of fat-splitting microbes occurs in a medium containing only fat as source of carbon and ammonium chloratum as source of nitrogen.

B. Denitrification with fats.

In our researches on denitrification with fats no other source of carbon was present in the medium composed of 100 tapwater, 1 kaliumnitrate, 0,05 bikaliumphosphate.

The culture was arranged as follows: about a gram of fat was melted in a carefully dried stoppered bottle with narrow mounth of ± 250 c.c. capacity; by turning the fat is evenly distributed over the inner surface. After cooling the bottle is filled with the said nutrient liquid which is subsequently inoculated with garden soil or some other infection material.

A series of experiments at temperatures between 20° and 45° C. proved that at 27° 30° C. the strongest denitrification was brought about; at this temperature the subsequent researches have been made.

If we inoculate with 3 grams of garden soil, sewage- or canal mud and cultivate at ± 28°, we see after one or two days the topmost edge of the fat layer near the stopper grow white. From here the decoloration proceeds to the bottom of the bottle. Soon gas bubbles arise from the inner wall of the fat layer, then they also form between the fat and the glass wall, by which the fat is separated from the glass. After 5 or 6 days we usually see the pieces of fat partly lying at the bottom. The fat, at first rather transparent, grows white, then dirty yellow and quite opaque. The culture liquid, partly pressed out of the bottle, is turbid and dirty yellow. Transplantations of such a culture to a fresh medium, arranged in the same way, yield again a good growth, whereby the described changes of fat and culture liquid return.

The bacteria which cause the denitrification with fat may be studied better by sowing the culture on broth gelatine or tapwater gelatine with addition of 0,5 °/₀ tributyrine, 0,05 °/₀ K_2HPO_4, and 0,1 °/₀ KNO_3 or NH_4Cl.

On the two plates the same species of bacteria develop, but they thrive better on broth gelatine than on the other medium.

The most vigorous bacteria denitrifying with fat proved to be *B. Stutzeri* L and N, *B. pyocyaneum*, *B. punctatum*, and a bacterium producing lipase and diastase, a representative of *B. denitro fluorescens non-liquefaciens*, described by VAN ITERSON [1]).

By cultivation at ± 20° the denitrifying species are more obvious, whereas at ± 34° the same flora appears as at 28°, but the growth is less vigorous; *B. sphaerosporus* and *B. nitroxos* described by BEIJERINCK [2]) denitrify neither with fat nor with glycerin or fatty acid.

The varieties of *B. Stutzeri* and *B. denitrofluor. non-liq.* are characterised as well by the different structure of their colonies as by their different power of denitrification and fat-splitting.

The above mentioned microbes denitrify with glucose, fatty acid, calcium lactate, humate of natron, asparagine and peptone. The various stocks of *B. Stutzeri* denitrify besides with maltose, glycerin, glycol and mannite, aethylacetate, maltose and butylalcohol; no acid is formed from saccharose, lactose and raffinose.

B. denitro fluor. non-liq. produces a little acid from glucose, but none from any of the said compounds; nor does it denitrify with mannite, glycerin, maltose, or glycol.

The fat-splitting of both bacteria under aërobic conditions was ascertained by cultivation in an ERLENMEIJER flask of 300 cc. with the culture liquid : 200 cc. tapwater, 1 gr. finely divided fat, 0.1 gr. ammonium chloratum, 0.1 gr. bikaliumphosphate and 0.5 gr. chalk.

After inoculation with 5 cc. of a 48 hours old brothpeptone culture of these bacteria, after 30 days at 28° C.

B. Stutzeri . . . . . . had split 630 mG. and assimilated 65 mG.
B. den. fluor. n. liq. had split 920 mG. and assimilated 80 mG.

These experiments show that by *B. Stutzeri* and *B. denitrofluor. non liq.* respectively 70 °/₀ and 100 °/₀ of the fat are split and

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[1]) Accumulation experiments with denitrifying bacteria. Royal Ac. 1902.

[2]) Bildung und Verbrauch von Stickoxydul durch Bakterien. Centralbl. f. Bakt. Abt. 2, Bd. 25, S. 30.

that nearly $^1/_{10}$ is assimilated for the building of the bacterial bodies.

Splitting and assimilation of fat at the denitrification were determined as follows.

In an ERLENMEYER flask of 300 cc. capacity a certain quantity of fat was weighed and the flask closed with a rubber stopper, fitted with a bent glass tube for gas outflow. After the apparatus had been sterilised and heated the fat was spread over the inner surface by rotation. After cooling 300 cc. of the following nutrient liquid was introduced: 100 tapwater, 1 kaliumnitrate, 0,05 bikaliumphosphate; inoculation took place with one of the denitrifying bacteria. The cultivation took place at 28° the evolving gases were caught over paraffin oil or caustic alkali.

Before the evolving of gas begins the oxygen above the culture is assimilated, the fat first undergoing hydrolytic splitting.

From June 28, 1909 to July 8 *B. denitrofluor. non liq.* formed 57 cc. nitrogen and 1.5 cc. carbonic acid with 0.4385 gr. of fat. The rapidity of the process had then decreased so much that it was resolved cautiously to renew the culture liquid without loss of fat. The decanted liquid reacted feebly alkaline, and contained nitrate, nitrite and glycerin, whilst per 25 cc. liquid 5.1 cc. carbonic acid was present. After the refreshing the fermentation velocity increased again, thereupon it decreased slowly. The total production until August 18 with the 0.4385 gr. of fat that had nearly disappeared, was 230 cc. nitrogen and 142.6 carbonic acid. If we neglect the very slight quantity of the still present saponaceous substances, about $^1/_6$ of the carbon of the fat is transformed by the denitrification into carbonic acid and $\pm ^5/_6$ into bacterial matter and insoluble organic compounds. In the culture liquid no intermediate products could be pointed out; evidently, also in this process the oxydation of the fatty acid only produces carbonic acid and water.

In Pl. 4 fig. 4 the rate of rapidity of the process is graphically represented. The evolved gas volumina per 6 hour's, cultivation are noted on the abscis; one centimeter representing a cm.^{3} of gas. On the ordinate the time is noted, one day being represented by one cm. We can very well perceive the increase in rapidity of the gas production after the refreshing of the culture liquid on July 8; yet the angle of inclination of the line is much smaller than that at the beginning of the process.

The cause of this falling must not be attributed to the formation of soluble secretion products of the culture, as is often the case in bacterial cultures, but to the presence of a thick layer of bacterial slime which has set off on the fat. This disturbs the movement of the substances and retards the rapidity of the process.

A denitrification by *B. Stutzeri* was set up in a similar way with 0.547 gr. of fat: the evolved gases were collected above caustic alkali, the medium was not renewed. From 9 to 28 October 1909 102 cc. of nitrogen were caught; on the 28th of October the fermentation produced less than a half cc. of gas per 24 hours, hence the experiment was stopped although part of the fat was still present.

In fig. 5 the rate of velocity of the gas evolution is represented in a way similar to that of the previous experiment.

Denitrifications with fatty acids proceed correspondingly to those with fats; on the other hand, denitrification with glycerin by *B. Stutzeri* occurs rapidly and completely; it is quite finished within a few days. About $^2/_3$ of the carbon of the glycerin is then converted into carbonic acid and $^1/_3$ is assimilated for the building up of organic material.

IV. FAT-SPLITTING BACTERIA IN MILK.

Milk belongs to the most favourable culture media for fat-splitting microbes; beside a finely divided and very easily saponifying fat, it contains excellent sources of nitrogen and carbon for these bacteria.

The number of fat-splitting organisms varies exceedingly in spontaneously infected milk, some hours after the milking we can already point out from 180—20000 per cc., among which may occur the species mentioned above.

Two factors chiefly influence the growth of fat-splitting bacteria in milk, namely temperature and admission of oxygen.

If we wish to accumulate fat-splitting microbes in milk the surest way is by aërobic culture at 10°—15°; at which grow chiefly *fluorescents*, *B. punctatum*, *micrococci* and so-called *aromatic bacteria* [1]). Also at aërobic cultivation at 27°—30° a considerable growth of fat-splitting microbes may occur, but this depends on the primitive composition of the bacterial mixture. At anaërobic cultivation, however, the lactic acid ferments in a short time overgrow all other species.

In connection with the lactic acid ferments we can admit as a general rule that the conditions of growth for fat-splitting organisms in milk are wholly opposed to those wanted for the thriving of lactic acid ferments.

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[1]) BEIJERINCK. Fermentation lactique dans le lait. Archives Néerl. des Sciences exactes et naturelles Serie II, 1. XIII.

VAN DER LEK. Aromabildende Bakt. in Milch. Centralbl. f. Bakt. B. 17.

In fig. 6 we see the rate of development of fat-splitting and that of the lactic acid ferments in milk kept under circumstances of temperature and oxygen pressure, such as is usually done in practice. (On the abscis 100 million bacteria are represented by one cm., on the ordinate 24 hours by 1 cm.). For this a 1 liter flask of 800 cc. of good clean milk was kept in a cellar at ± 10°; after every 24 hours the number of lactic acid ferments and that of the fat-splitting microbes was determined.

The bacterial ciphers used to construct the graphies, show that the proportion of the lactic acid ferments to the fat-splitting bacteria in the milk at the beginning was $^2/_3$; that same day after 8 hours $^9/_{10}$ and the 7 following days respectively $^3/_1$, $^5/_1$, $^{12}/_1$, $^{17}/_1$, $^{25}/_1$, $^{100}/_1$, $^{106}/_1$. During the first five days the number of fat-splitting microbes increased, but less rapidly than that of the lactic acid ferments; thereupon a relatively rapid destruction takes place at an acid degree of ± 85. The regularly increasing rate of acid appears to do little harm to the lipase producing bacteria, so sensitive to acidity, although these at a direct inoculation into acid milk, titrating 50 cc. $^1/_{10}$ N per 100 cc., no more grow; hence it is evident that they adapt themselves to the acid degree. To the fat-splitting species in this milk belonged: *fluorescents*, *micrococci* and the group of *B. lipolyticum*, described page 674.

The bacteria of putrefaction happening to get into the milk with the faeces of the cows or from the air of the stable, contain for the greater part lipolytic enzymes as for instance the aërobic species *B. vulgare*, *B. prodigiosum*, *B. fluorescens liquefaciens*, *B. pyocyaneum* and the anaërobic *Bacillus putrificus*, which last species is often met with in pasteurised milk.

The changes provoked in milk by the fat-splitting microbes are, excepting those caused by the lipolytic influence of the microbes, more particularly to be ascribed to their peptonising action. To milk they give a cheesy or soapy smell and often a bitter taste; they cause rapid creaming and render the suspended fat rancid as also the butter made from it.

Hence we must consider these bacteria as the most dreaded enemies of the dairy- and fat industry.

SUMMARY.

1. The fat-splitting power of aërobic as well as of anaërobic micro-organisms and their power of denitrifying with fat, may in a simple way be determined by means of fatted test-tubes.

2. By a large number of bacteria, universally spread in nature, fats may be broken off anaërobically, oxydised aërobically, or if nitrates or nitrites are present be denitrified.

3. All these processes are caused by the secretion of "lipase" by microbes; glycerin and fatty acids separated by the action of this enzyme are then further converted by the organisms.

4. Several fat-splitting organisms produce two lipases, α- and β-lipase; the former diffuses more rapidly than the latter and splits fat as well in an acid as in an alkaline medium; β-lipase is formed in an acid medium but does not decompose fat in it; it may however, become active again after neutralisation of the medium.

5. Lipase diffuses through water-free fat; but the diffusion velocity is very small.

6. The aërobic fat-splitting bacteria thrive well in culture media containing exclusively fat as source of carbon and ammonium chloratum as source of nitrogen.

7. To the already known fat-splitting bacteria we can add: *Bacillus putrificus* (Bienstock), a representative of the *mesentericus group*, *B. Stutzeri*, and *B. denitro fluorescens non-liquefaciens*.

8. Milk is a favourable medium for fat-splitting microbes.

9. In spontaneously infected milk, kept under circumstances usual in practice, growth and destruction of fat-splitting bacteria and lactic acid ferments occur about simultaneously; they are chiefly dependent on the acid production.

10. The injurious influence of fat-splitting microbes on the quality of dairy products is chiefly owing, besides to their lipolytic properties, to the formation of bitter tasting and badly smelling products from proteids and casein by these microbes.

This subject will be more elaborately treated in the "Centralblatt für Bakteriologie".

Botany. — *"On the cause of dimorphism in Oenothera nanella."* By H. H. Zeijlstra Fzn. (Communicated by Professor Hugo de Vries).

In 1905 I occupied myself with an investigation of the dimorphism of *Oenothera nanella* which in consequence of many other duties before my departure to India, could not be completed. Although I intend to continue this inquiry next year, I think it desirable already to communicate the following preliminary results.

In "die Mutationstheorie" de Vries in a description of the species of *Oenothera* arisen by mutation has made us acquainted with a dwarf-form, which already occurred at the beginning of his experiments in 1888. It has since shown itself each time that a sufficiently large number of plants has been worked with.

De Vries named this plant *Oenothera Lamarckiana nanella*, or rather, briefly, *Oenothera nanella*, because, although the *nana*-characteristic can occur in species of the most diverse orders, yet this *Oenothera* with regard to its constancy on sowing can in no respect be distinguished from an elementary species.

Not only from *Oenothera Lamarckiana*, but also from *Oenothera laevifolia*, *O. scintillans*, *O. leptocarpa*, and from hybrids of *Oenothera Lamarckiana*, with the new species, *Oenothera nanella* appeared quite uniformly. On the average $^{1}/_{2}$ $^{0}/_{0}$ of the plants showed the dwarf-type.

The *nanella* can already be recognized as a seedling by the two first leaves, which are broad and have a short petiole. Then follow 2—4 leaves with long petioles, which resemble more the *Lamarckiana*-type; de Vries regards their appearance as an atavism.

As a rule *Oenothera nanella* is an annual. In this case the ascending stem grows out at once; in plants which will be biennials, several broad radical leaves with short petiole are developed, so that the plant hibernates with a dwarf rosette.

The fully grown stem has remarkably short internodes. This, in addition to the broad shape of the leaves, gives the plant a very squat appearance.

In spite of the small size of the plant, its flowers and fruits are hardly smaller than those of *Lamarckiana* It sometimes happens that a plant bears these flowers when the shoot is no more than 10 cm. high.

This very characteristic form showed itself through mutation about 400 times in 80.000 plants. Its constancy was carefully and repeatedly tested.

In 1893 some *nanellas*, of which the ancestors had arisen in 1889 as mutants from *Oenothera laevifolia*, were pollinated with their own pollen. The seed yielded 440 plants, all of which bore the *nanella*-characteristic.

In 1895 twenty *nanellas* were treated in the same way, they themselves having occurred as mutants from *Lamarckiana*. They yielded 2463 descendants: all were *nanellas*.

The experiment was performed in 1896 with 18000 plants and the same favourable result was obtained. Three seedlings showed simultaneously with the *nanella* characteristics, those of *Oenothera oblonga* and one those of *O. elliptica*.

From these experiments the conclusion was drawn that *Oenothera nanella* when it appears through sowing is at once perfectly constant.

In 1905, among the *nanellas*, some plants were found, which, although dwarfs, differed from the form just described by possessing elongated internodes and narrow petiolated leaves. At the same time there were plants which, in addition to these elongated shoots, bore one or more compact branches.

In comparison with the new form, the first has an unmistakably malformed appearance. The question therefore rises to the forefront whether possibly the dimorphism of stem and leaves must be attributed to the influence of organisms in the body of the plants. An aberration which often occurs in the floral buds of *Oenothera nanella*, and the course of which is accurately described in "die Mutationstheorie", gives powerful support to a belief in a parasite, which cannot kill the plant, but which nevertheless greatly hinders its development.

"Auf einjährigen Exemplaren sind die Blüthen vielfach unvollständiger Ausbildung ausgesetzt. Aber meist nur eine oder wenige Blumen pro Pflanze. Bisweilen fehlt der Blüthenstaub oder er ist nur in spärlicher Menge entwickelt; ziemlich oft können die Narben sich nicht öffnen und bleiben somit zu einem vierseitig-conischen Gebilde zusammengefügt. Dieses Gebilde ist oft nur sehr klein und so schwach, dass es vor der Bestäubung sich schwärzt und vertrocknet. Oder der Griffel ist zu kurz, bisweilen kaum aus der Blüthenröhre hervorragend.

"Sehr auffallend ist der schiefe Stand der Blüthenknospen auf den Kelchröhren. Die Kelchzipfel mitsammt der Krone sind dann an ihrem Grunde gebogen; im ersteren Fall derart, dass sie senkrecht auf der Röhre stehen. Das Oeffnen des Kelches ist dadurch erschwert und geht in abnormaler, oft mangelhafter Weise vor sich. Die Blumenblätter entfalten sich unvollständig und die Geschlechtstheile sind meist mehr oder weniger steril.

"Alle diese Abweichungen sieht man namentlich an den untersten Blüthen der Traube, zumal wenn die Pflanze bereits bei einer Stengelhöhe von 10—15 cm. zu blühen anfängt. Aber auch bei der gewöhnlichen *Lamarckiana* misslingen oft mehrere von den untersten Blüthen. *Wächst die Nanella durch diese Periode hindurch und wird sie dabei auffallend kräftiger, so bildet sich nach einer kürzeren oder längeren blüthenlosen Zwischenstrecke in der Traube meist eine volle und schöne Krone grosser Blumen aus. Diese erhebt sich auf dem dürren, wenig beblätterten blüthenlosen Stengeltheil hoch über die* *untere Hälfte der Inflorescenz empor. Aber bei Weitem nicht alle Individuen werden hinreichend stark, um solches zu erreichen.*

"Handelt es sich somit darum, die Zwerge in möglichst schöner Entwickelung und voller Blüthenpracht zu cultiviren, so empfiehlt es sich, sie stets durch späte Aussaat zu zweijährigen Exemplaren zu erziehen". [1])

It can be seen from the italicised portion of the above quotation that, considered objectively, the squat-shaped *Oenothera nanella* behaves as if in its development it has a resistance to overcome. If it succeeds in this, a normal apex is formed on the infloresence.

If the stem of a malformed *nanella* is cut through, one finds in part of the section the elements in groups filled with a black mass. This is most plainly shown in the elements of the secondary wood; these are often in a transverse section wholly black internally. This filling is found not only in the wood fibres, but also in the medullary ray cells; the wood-vessels are not as a rule wholly filled, but a similar substance lies here along the wall in the shape of a segment. The same applies to the cells of the pith, the cortex-parenchyma, the collenchyma and the epidermis. Nevertheless wholly filled cells can also be found in the cortex-parenchyma.

This phenomenon appears in the same way in the root of *Oenothera nanella*.

On looking at a section under a high power the black mass resolves itself into a large number of black spots which are evidently imbedded in a gelatinous matrix. With sufficiently strong magnification, especially where the mass of cells which have been cut through, has spread more or less over the preparation, places are readily found, where the black dots lie so far apart that they can be made out separately.

Every individual is surrounded by a lighter zone. The individuals are partly arranged in pairs or in fours, and are not of equally dark colour; the greater number are however opaque in the strongest illumination.

The external characteristics leave no doubt that the organism seen in the tissue of *Oenothera nanella* is a bacterium of the genus *Micrococcus*. It does not differ from the *Micrococcus* in tooth-mucilage either in shape or size, though it is as a rule darker in colour.

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[1]) Die Mutationstheorie, Bd. I. p. 267 and 268.

In the English edition is added Vol. I. p. 376: "These and other malformations of the dwarfs are often due to a disease and as such to a large degree dependent on outer circumstances; (note of 1908)".

This note is based on the investigation here published.

It would appear that the *Micrococcus* forms a zoogloea, which fills the whole fibre or cell. There is, as a rule, in the preparations, a space between the cell-wall and its contents, though the latter has often so exactly the same polygonal outline as the cell, that there can be little doubt that the contents only retracted from the wall in the making of the preparation.

Other organisms than the *Micrococcus* have not up to the present been found.

Although therefore on the one hand *Oenothera nanella* with its contracted shoots has the appearance of a diseased plant, and on the other hand there is found in its tissues an organism, that may very well be the cause of the disease proof remains to be given, that *Micrococcus* is indeed the agent producing the malformation. At the same time the question waits for a further answer, how it can be explained that on the origin by mutation of *Oenothera nanella* the diseased form always occurred and that the first normal plant was only obtained many years later.

The appended figure of an *Oenothera nanella* with two kinds of shoots was prepared from a photograph made on the 27th of Sept. 1905 in the Botanic Garden at Amsterdam from a fully grown plant.

The shoot on the extreme right was 33 c.m. high. In the middle a diseased shoot is seen, with closely packed leaves. The top of this shoot is added from another specimen drawn from nature, in order to show the difference between normal and abnormal flower buds.

In the diseased shoot, the calyx-tube is curved, so that the calyx and the corolla make almost a right angle with the axis of the ovary, whilst in the normal shoot the different parts of the floral bud lie in one straight line.

The diseased shoots have much shorter and thicker internodes than the healthy shoots.

The leaves of the true *Oenothera nanella* completely resemble those of *O. Lamarckiana*, except for the size. Those of the aberrant shoots are on the contrary provided with very short brittle petioles and broad short laminae.

Healthy shoots have up to the present only been observed exceptionally. The reason is partly to be found in the fact that the normal *nanella* wholly resembles a dwarf *Lamarckiana*, and in the method employed, of examination as young seedlings, can be mistaken for the latter.

On the other hand we must take into account, that attempts to obtain seed from healthy shoots have been unsuccessful. These shoots generally appear later on the plant and bloom too late for their fruits to mature. The *nanellas* obtained from seed have therefore all had diseased parents, and the possibility is not excluded, that they may have received from their parents, if not the *Micrococcus* itself, yet the susceptibility to the attacks of this organism.

As long as we have not succeeded in growing perfectly healthy *nanellas*, we cannot determine by infection experiments whether the *Micrococcus* is indeed the cause of the pathological phenomenon.

EXPLANATION OF PLATE.

Fig. 1. *Oenothera nanella*, dimorphous plant (× $^2/_3$).
Fig. 2. Transverse section through the stem, near the cambium (× 555).
Fig. 3. Transverse section through the stem : a few wood fibres near the primary wood (× 1730).

Chemistry. — "*The synthesis of as. heptachloropropane from tetrachloro-ethylene and chloroform with the co-operation of aluminium chloride.*" By Prof. J. Böeseken and Dr. H. J. Prins. (Communicated by Prof. S. Hoogewerff).

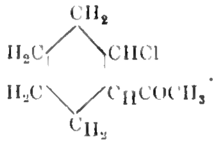
In a previous research by one of us (Recueil XXIX p. 109 (1910)) it was found that dichloroacetyl chloride is decomposed by aluminium chloride in two directions. Firstly it decomposed into chloroform and carbon monoxide; secondly, besides carbon monoxide and hydrochloric acid a beautifully crystallised product was obtained melting at 32° to which, provisionally, the composition C_5Cl_{10} was assigned. In the meanwhile we have succeeded in conducting the decomposition in such a manner that a large quantity of this substance was obtained, thus enabling us to study some of its decomposition products. From this research it follows that the substance is identical with the as. heptachloropropane obtained by Fritsch (Ann. **297** [1897] pg. 312) from pentachloroacetone and phosphorus pentachloride as shown by the subjoined table.

While we were engaged in studying the question as to how heptachloropropane was formed from dichloroacetylchloride, one of us (Pr.) succeeded in obtaining a very good yield of this chloride by direct addition of chloroform to tetrachloroaethylene under the influence of aluminium chloride. If these chlorides are boiled together for some time in a reflux apparatus, the ethylene perchloride is almost entirely converted into heptachloropropane.

It should be observed, that neither chloroform, nor ethylene tetrachloride, nor the end product C_3Cl_7H combine with the aluminium

	m. p.	b. p.	Analyses		Decomposition with $NaOC_2H_5$ to hexachloropropylene
Product from $CHCl_2COCl$ and $AlCl_3$ (B. and Pr.)	32° Solidifying point 29,95°	132° at 30 mm 147° „ 43 „	C = 12.95 and 13.03 H = 0.52 „ 0.27 Cl = 86.60 „ 86.56	Calculated C = 12.61 H = 0.33 Cl = 87.06	With 1 mol. was formed an oil having an odour of fruits, which possessed all the properties of the C_3Cl_6 prepared by FRITSCH. B. p, 209°.
$CHCl_2CCl_2CCl_3$ (FRITSCH)	30°	150-151° at 50 mm	Cl = 86.8		With 1 mol. was formed an oil having the odour of raspberries Cl_3Cl_6. B.p. 209 2 0 , which with three more mols. was converted into the ortho ester of trichloracrylic acid.

chloride. A little of the catalyst dissolves in C_2Cl_4, but an additive product cannot be isolated. [Aluminium chloride may be readily recrystallised from C_2Cl_4 by heating it with the solvent to 130°—140° in a sealed tube. On cooling it is obtained in large six-sided crystal plates which after having been washed with carbon tetrachloride and dried by suction, do not contain any carbon].

This simple synthesis not only elucidates the progressive change of the reaction of FRIEDEL and CRAFTS, but it throws an important light on the catalytic action of aluminium chloride, as it gives an additional proof that the theory of the intermediate products for the "explanation" of this action must be abandoned, which one of us has already argued many a time. As regards the first point, I refer to the researches of KRAPIWIN (Centr. Blatt I. p. 1335) and of DARZENS (Compt. Rend. **150** p. 707). The first has built up unsaturated ketones from acid-chlorides and from unsaturated aliphathic hydrocarbons by means of aluminium chloride. The latter has prepared, in the same manner, acetyltetrahydrobenzene from tetrahydrobenzene and demonstrated also that in this reaction a hydrochloride is formed as an intermediate product, of which it is assumed without further proof that it should have the composition .

From these observations it appears that, in the condensation, there must be present an unsaturated compound and another substance (generally a chloride); and from our synthesis the conclusion may be drawn that indeed, the chloride (chloroform in this case) is split and that the parts are taken up by the double bond (that of ethylene perchloride in this case). Then the reaction ceases because heptachloropropane is a stable compound[1]).

As regards the second point there are no indications of intermediate products (see also the investigations of MENSCHUTKIN, who also was unable to obtain additive products of benzene-hydrocarbons with aluminium chloride Cent. Blatt. 1910, I. p. 168); the most important catalytic action must, therefore, take place during the first stage of the reaction viz. the moment that the molecules present come under the influence of the catalyst. This may be explained in the most simple manner by assuming that aluminium chloride renders the chloroform active in such a manner that the molecular parts $CHCl_2$ and Cl can attach themselves to the double bond of the ethylene perchloride also rendered active.

We have proved in the second place that pentachloroethane also readily yields as. heptachloropropane with chloroform and aluminium chloride. As C_2Cl_5H is split by aluminium chloride, at the boiling point of chloroform, into C_2Cl_4 and HCl (also compare MOUNEYRAT Bull. [3] **19** p. 179) this condensation may now be explained in a very simple manner: pentachloroethane loses C_2Cl_4 and this takes up chloroform. This synthesis is interesting because we are dealing here with the succession of two very simple cases of the reaction of FRIEDEL and CRAFTS (Recueil **29** (1910) p. 92)

$$\text{I} \quad C_2Cl_5H \rightarrow HCl + C_2Cl_4 \quad ; \quad \text{II} \quad CHCl_3 + C_2Cl_4 = C_3Cl_7H$$

In case I the chloride is rendered so active that decomposition sets in; in case II the chloride is rendered active but not decomposed.

The investigation of the ethane chlorides is being continued in various directions; the results will be published elsewhere.

Org. Chem. Lab. Techn. University.

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1) It should be pointed out here that, through these investigations, the proof has been furnished that no essential difference exists, in regard to the reaction of FRIEDEL and CRAFTS, between benzene and other unsaturated compounds.

Physiology. — "*On the physiological effects of derrid.*" By E. H. van Hasselt, Surgeon in the Dutch Colonial Army, Assistant at the Pharmacological Institute at Utrecht. (Communicated by Prof. H. Zwaardemaker).

(Communicated in the meeting of November 26, 1910).

Toebo, also called *toeba* or *toewa*, is a collective name for several vegetable poisons [1]; it is also called *akar djenoe* [2]. The *toeba* we mean here is derived from Derris elliptica Benth., a tropical climbing-plant belonging to the family of the Papilionaceae, the roots of which are very poisonous. In an illustrated work [3] of his, Greshoff has given a picture and a description of this plant. It grows in British-India, Indo-China, and the Indian Archipelago, and is also cultivated there (e. g. in Western Java). The roots are especially used for catching fish. They are bound together in large bundles and taken down the river in boats by men, women, and children; at a favourable spot the roots are squashed and thrown into the water and soon after this the fishes rise to the surface intoxicated and are caught with the hand, in nets or also by means of harpoons [4]. The savage tribes of Malacca use as an arrow-poison [5] the *toeba*, which has been decocted together with parts of various kinds of antiaris and strychnos; often arsenic is added to this decoction. Then the arrows are dipped into it, dried and shot from a blowpipe. Among the Dajaks these arrow-poisons are known as *Ipoe* or *Siren* [6]. A watery extract of the roots is used for exterminating insects.

About this remarkable plant Greshoff tells us as follows [7]:

"At first the taste of the roots of this plant is slightly aromatic and astringent; afterwards remarkably anaesthetic, reminding one of cocaine, but with this difference that the taste has not entirely disappeared and that a peculiar feeling of cold is observed in the palate; moreover, on account of the diminished sensitiveness of the mucous membranes, it is as if one has a swollen tongue, which feeling is also experienced when speaking. This sensation continues for hours, sometimes for days. In the beginning there is an increased

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[1] Dr. C. L. v. d. Burg. De voeding in Ned. Ind. Amst. 1904. p. 78.

[2] Indische Vergiftrapporten, den Haag 1902. p. 25. — De Clercq. Nieuw plantk. woordenb. voor Ned. Ind. Amst. 1909. p. 219.

[3] Greshoff. Schetsen van nuttige Ind. planten. 3e Afl. No. 25.

[4] Dr. A. W. Nieuwenhuis. Quer durch Borneo. I. Leiden 1907.

[5] Lewin. Die Pfeilgifte, Berlin 1894. p. 98.

[6] Geneesk. tijdschr. v. Ned. Ind. VII. 1859 p. 332.

[7] Greshoff. Mededeel. 's Lands Plantentuin VII. Batavia 1890 p. 12

saliva-secretion. Some people complain of head-ache after chewing the root."

He has examined the effect on fishes by putting goldfishes into a decoction of the roots of 1 : 2500; after 3 min. they were lying at the bottom, intoxicated, breathing feebly, and they died though put in fresh water. In a decoction 1 : 25000 complete narcosis manifested itself within 5 minutes. The bark of the root appeared to be more poisonous still; in a decoction 1 : 300000 small sawah-fishes [1]) were intoxicated within $^3/_4$ hour and they died within 24 hours. GRESHOFF [2]) succeeded in extracting from the roots of Derris elliptica its active element *derrid,* and found that goldfishes died within half an hour in a solution 1 : 5.000.000, after a period of intoxication. He says [3]): "It seems more likely to me that derrid has a specific influence on the central nervous system of fishes than that it acts as a poison on respiration by stopping the taking up of O or the giving up of CO_2 in the gills", and he thinks it will be very difficult to examine its effects on other animals than fishes, on account of its sparing solubility.

VAN SILLEVOLDT has chosen derrid as the subject for his dissertation, which he has worked out in the pharmaceutical laboratory at Leyden [4]). For the preparation of derrid he adopted GRESHOFF's method with some alterations for the purification. Now as for my experiments I have employed the preparation used by VAN SILLEVOLDT, which Prof. WIJSMAN was so kind as to place at my disposal; his way of proceeding will be mentioned here: The squashed roots were extracted with water, pressed and dried; then they were extracted with alcohol 96 %. This extract was evaporated with a little water down to a small volume and cooled, after which there appeared at the bottom of the vessel a resinous substance, which was washed with water and dried; this was raw derrid. This was purified by removing the greasy elements with petroleum-ether and by shaking the insoluble derrid with $^1/_2$% KOH; then it was dissolved in ether and precipitated again with petroleum-ether. The first precipitations were strongly coloured and crystalline; afterwards a white amorphous substance appeared. When filtered, this substance was dissolved in ether, and while heated, petroleum-ether was added to it; then it was cooled down and a yellowish-white matter was formed, pure derrid.

This derrid is insoluble in water; very sparingly soluble in petroleum-ether; very easily in chloroform; easily in ether, alcohol, acetic acid, benzene, acetone, carbon disulphide and ethyl acetate. Very little can

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[1]) A *sawah* is an Indian watered ricefield.

[2]) GRESHOFF, Med. XXV. Den Haag, 1898, p. 49.

[3]) GRESHOFF, l.c p. 17.

[4]) VAN SILLEVOLDT, Ueber das Derrid und das Pachyrhizid. Diss. Marburg 1899.

be dissolved in 10 % KOH, from which it can be precipitated again with acids. Together with water the alcoholic solution gives an emulsion, in which microscopical amorphous particles and masses are to be seen. The formula is $C_{33} H_{30} O_{10}$; glucoside-properties are not present. VAN SILLEVOLDT has also made experiments on fishes and found as follows: Minnows (Gasterosteus pungitius) died in a dilution 1 : 6.000.000 within 30 min., after a period of great agitation, followed by intoxication. Frogs, subcutaneously injected with 3 m.g. derrid were quite paralysed after 24 hours, without convulsions having manifested themselves. I shall now mention my own experiments.

Effect of derrid on fishes.

Minnows (Gasterosteus pungitius) were put in the following fluids: In 1 L. of water, to which was added 10 cc. standard solution (derrid 10 m.g.; alcohol abs. 5 cc.; water 95 cc.), which corresponds with a dilution of 1 : 1,000.000. As soon as a fish came into the water, it went down to the bottom of the glass, remained motionless there for some moments, soon became agitated and swam quickly to and fro, up and down; its gill-flaps opened wide and moved rapidly, much more rapidly and intensely than with the "normal fish" (one that had been placed in an equal quantity of water with alcohol). The fish showed violent dyspnoea, jumped out of the water after 6 min., fell continually on its side and soon lost its balance altogether; tumbling round and round it sank down to the bottom, where it remained; then it shot up to the surface again as swift as an arrow, only to come down again soon after that. After 15 min. it was lying on its side at the bottom of the glass, in violent dyspnoea; once again it swam rapidly to the surface, but soon after it was lying again at the bottom, with limp fins and quite unconscious. After 20 min. its respiration became irregular, less and less frequent and after 28 min. it ceased altogether.

The same experiment was made with dilutions 1 : 2.500.000; 1 : 5.000.000 down to 1 : 10.000.000, the latter being lethal within 27 hours. In the strong dilutions the symptoms did not manifest themselves until very late; then suddenly intoxication followed and soon after this death.

The "normal-fish" seemed in good health. It further appeared that, as soon as the first symptoms of agitation had clearly manifested themselves, the fish could not be saved if put in fresh water.

From these experiments it appears that an effect on the central nervous system seems very probable and specially on the respiratory-centre.

As the standard-solution was frothing very much, derrid might belong to the saponins and as such cause laking of the blood.

Effect on blood.

Derrid was added to a solution of rabbit's blood and the spectra were observed. From this it appeared that the normal oxyhaemoglobin-spectrum was unchanged; when nitris amylicus was added the methaemoglobin-spectrum showed itself and when it was reduced with STOKE's solution, the haemoglobin-band appeared. A bottle with blood-solution, quite full and well corked, was put aside after derrid had been added and after the presence of oxyhaemoglobin-bands had been ascertained. After more than 36 hours haemoglobin had formed, which was apparent from the spectrum, whereas after shaking the bottle both the oxyhaemoglobin-bands reappeared. So this proves that derrid does not change the power of haemoglobin to easily take up and give up oxygen.

A series of experiments on laking was made.

1. The blood of the minnow that died during the first experiment was received in a physiological salt solution; no laking showed itself here.

2. Eel's blood was defibrinated, washed and the standard solution was added to it (per cc. 0,1 m.g. derrid and 0,03 cc. alc. abs.); the "normal fluid" was a corresponding alcohol solution. By addition of NaCl [1]) both solutions were made isotonic to the blood. In each of a row of test-tubes was put 1 cc. blood besides increasing quantities of derrid and alcohol, in such a way that each tube contained an equal quantity of alcohol and cc. fluid, so that only the quantity of derrid varied. The quantity of derrid was such that effect on the whole animal could be expected with absolute certainty; a tube with blood and salt-solution was always at hand for the sake of comparison.

After 12 hours neither laking nor agglutination was to be observed. Then in each of the tubes was put a quantity of saponin corresponding in weight to the lowest quantity of derrid of all the tubes: after 3 min. laking manifested itself very clearly.

3. Blood of a cat was treated as stated above and placed in a thermostat at 37°. Then it appeared that neither laking nor agglutination could be observed, even after 19 hours. In a subsequent series of experiments, after 4 hours, laking manifested itself in 2 out of the 12 tubes, but these tubes contained the smallest quantity of derrid, so that action of alcohol must be looked upon as the cause.

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[1]) The NaCl was added to the solution immediately before using it because derrid is precipitated soon after the addition of NaCl.

4. Experiment on blood of a guinea-pig, as stated above; after 18 hours nothing could be observed; after 20 hours there was laking in all tubes, including the tube with the "normal fluid".

5. Cow's blood was treated in the same way; after 20 hours neither laking nor agglutination could be found.

6. The same negative result can be mentioned of human blood: no laking or agglutination after 19 hours.

From all this it appears that derrid has neither a laking nor an agglutinating effect on the blood of the above-mentioned animals, and that in the cases where laking had manifested itself, this must be put down to action of alcohol or the long duration of the experiment.

Effect on respiration.

This effect was studied from the surviving eel's head which, according to Kouliabko's method [1]), was prepared and nailed on to a board. In the hepathic vein was tied a cannula, through which Ringer-Locke's solution, with or without derrid, could be led from 2 Mariotte bottles. The "derrid solution" was a dilution of 1 : 1.000.000; to the "normal solution" was added a quantity of alcohol and NaCl equal to that already being in the "derrid solution". The respiration and the movements of the heart were registered on the kymograph. On addition of derrid convulsions of the muscles of the whole head manifested themselves in fits and, independent of these, also intensified movements of the gills; after continued action these movements stopped, as well as the convulsions. So here we have a poison first stimulating and then paralysing the central nervous system, and especially the respiratory-centre.

When frogs were subcutaneously injected with derrid (0,5—6 mg.), respiration stopped, besides other symptoms that shall be mentioned below. Action of alcohol was excluded.

The same symptoms were observed with white mice that were subcutaneously injected with derrid (0,1—3 mg.).

Rabbits, injected with derrid in a vein of the ear (1.6 mg. per KG.), soon died through stopping of the breath; however, if immediately after this stopping of the breath tracheotomia and artificial respiration were performed, the animals lived, because after some time spontaneous respiration showed itself again; then the trachea and the wound were sewn up. This effect was further studied in the following manner: Rabbits were narcotised with urethane; then tracheotomia

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[1]) Kouliabko. Arch. Internat. de Physiol. Vol. IV 1906—1907 p. 437.

was performed, the cannula being connected by means of a T-tube with a MAREY tambour; a cannula was put in the jugular vein for injections and another was tied in the carotid artery to ascertain the blood-pressure by means of a mercury-monometer. The standard-solution contained 2 mg. per cc. After a sufficient normal-period 2 mg. derrid were injected into the jugular vein; soon deep respirations manifested themselves, ending in paralysis when a much greater dosis (= 4 mg.) was administered. Smaller doses only resulted in intensified respiration, which lasted for a considerable time.

In order to examine the changes of respiration more minutely, the delicate method of DRESER[1]) was applied. Here the animal breathes through a breathing-mask with minimum resistance and the expired air is received in an eudiometer and measured. The rate of the breath per minute, the volume per minute and per respiration, were calculated.

After a sufficient normal-period derrid was injected, the needle of a syringe having been put into a vein of the ear beforehand. It now appeared that the rate first increased, then decreased rapidly; that the volume per minute first increased and then decreased but little, and that the volume per respiration increased rapidly.

On further dosing respiration became irregular and feeble, and asphyxia followed soon after. So at first derrid strongly stimulates respiration; deepening of the respiration comes most to the fore, even so strongly that the quantity of air, inspired per minute, increases. This effect is already known of morphine and several of its derivatives and is a central one. When larger doses are administered the stimulation is followed by paralysis, resulting in death with warmblooded animals; if artificial respiration is applied it appears that this effect is a transient one and that the centre recovers itself after some time.

Effect on circulation.

During the above-mentioned experiment on the eel's head the following could be observed from the heart:

When after the normal-period derrid was added and the respiration was paralysed, irregularities showed themselves in the function of the heart, often resulting in long pauses; then slowing of the pulse was observed and dilatation, especially of the auricle. If the skull had been opened beforehand and the brain as well as the spinal cord destroyed, the same symptoms showed themselves, so that the cause must be put down to the circulation-apparatus itself. Therefore further

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[1]) DRESER. Pharmacol. Untersuch. üb. das Lobelin der Lobelia inflata. SCHMIEDEBERG's arch. 1890, n⁰. 26, S. 237.

experiments were made on the isolated heart. The heart was perfused with 0.9% NaCl (Kouliabko), then with derrid-salt-solution (1 : 1.000.000—1 : 30.000). First the ventricle, in later experiments also the auricle, was registered. Slowing of the pulse now showed itself again, dependent on the effect on the motor apparatus of the heart itself, for if atropin was added to the solution or dropped on to the heart, the slowing of the pulse was not neutralised, neither was it prevented. When the suspension method of auricle and ventricle was applied, it appeared that there was absence of every second ventricle contraction. I have not observed complete paralysis, nor when larger doses were administered.

In frogs the influence on the heart was also examined. After the above-mentioned injections the last symptom was heart-paralysis. Further experiments were made on the heart either isolated, or in situ perfused by a cannula tied in the sinus, or excised and attached to the Straub cannula [1]) so that it could go on beating unchanged for hours by means of Ringer solution (2 c.c.). If after the normal-period derrid was added, slowing of the pulse and irregularities showed themselves as before; at last the heart stopped in diastole. If for checking-purposes only 0.6% NaCl or Ringer's solution besides corresponding quantities of alcohol were added, this did result in slowing of the pulse and weakening of the heart, but never in irregularities if these had not manifested themselves from the beginning. If then derrid was added the irregularities appeared. Experiments were also made on the heart in situ; here a cannula was tied in the vena cava inferior through which the solution was admitted; the animal had been decerebrised and curarised beforehand. Ventricle and auricle were registered. Here also slowing of the pulse could be observed, besides absence of ventricle-systole, paralysis of the auricle and all kinds of irregularities. Destruction of brain and spinal cord, besides atropin, did not influence these symptoms. During a subsequent series of experiments ventricle and auricle were connected with the inductor and stimulated faradically and by single break induction shocks. Then it appeared that the refractory period of the ventricle was lengthened; the time of conduction from auricle to ventricle did not show any perceptible change.

Consequently the influence of derrid on the heart of frogs is a negative chrono-, bathmo-, and tonotropic one. The irregularity of the pulse, especially the absence of ventricle-systole and of every second

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[1]) W. Straub. Die Wirk. des Antiarins am ausgeschnittenen, suspendierten Froschherzen. Schmied arch. 1901. nr. 45, s. 346.

ventricle contraction, appears, at least partially, to be dependent on the lengthening of the refractory period, which has been demonstrated before by Straub with respect to the influence of antiarin on the heart. When white mice were subcutaneously injected, the last symptoms were heart-paralysis and irregularities; now ventricle and auricle beat in normal succession, now at the same time, sometimes in reversed succession; so besides the symptoms observed in the frogs we here find automatism of the ventricle, besides originating of the stimulus in the auriculo-ventricular zone. At last the heart stopped in diastole.

Further experiments were made on rabbits; during the above-mentioned experiments also the blood-pressure was recorded. On administration of derrid a fall of the bloodpressure immediately ensued, which recovered itself however, often to its normal height; after subsequent injections the bloodpressure fell more and more till at last heart-paralysis followed.

The dose required for heart-paralysis is much larger than that for respiration-paralysis, even amounts to four times as much. Slowing of the pulse always manifests itself here as well.

The above-mentioned symptoms were not influenced by cutting of the vagi, the sensitiveness of which appeared to remain unchanged.

Further experiments were made on the isolated heart. For this purpose the rabbit was narcotised with urethane and ether; thoracotomia was performed and both parts of the thorax were turned aside; ventricle and auricle were registered.

When derrid had caused stoppage of the breath, irregularities showed themselves in the function of the heart on further dosing; sometimes ventricle and auricle contracted by themselves; dilatatio cordis was ever present; the end was always paralysis.

To ascertain what was the cause of the fall in the bloodpressure, the following experiments were made: Of a rabbit in urethane-ethernarcosis that was afterwards curarised, the bloodpressure was registered as well as the oncometrical volume of the kidney or the intestine and that of a hind leg. It now appeared that after the injection of the poison into the jugular vein the bloodpressure decreased simultaneously with the volumina of kidney, intestine and leg; if the bloodpressure increased, these volumina did the same. The volumina of the organs therefore followed the changes of the bloodpressure quite passively, so that the fall of the bloodpressure did not result from active dilatation of the vessels but from weakening of the heart.

So from all these experiments it appears that derrid acts on circulation, yet not so intensely as on respiration. The changes in the circulation of the blood depend only or at least principally on the effect on the heart, the pulsations of which are weakened and become irregular; only very large doses are able to paralyse the heart definitely.

Effect on the intestine.

Pieces of intestine of cats were suspended in Ringer's fluid through which *O* was led, their contractions being graphically registered. Then the standard solution was poured into this fluid. The result was that paralysis always manifested itself but the doses required to bring this about varied a good deal. The largest dosis required was 2 mg. to 250 cc. fluid. Stimulation-symptoms in the beginning could not clearly be observed.

Effect on the mucous membranes and per os.

On the conjunctiva of a rabbit was put some derrid in substance and afterwards in solution; no symptoms manifested themselves. I myself put a piece of cotton-wool soaked in 0.2°/₀ derrid solution between my lips and one between cheek and gums.

After about half an hour I observed a peculiar tingling feeling in my lips and a sharp feeling in my throat as if I continually felt inclined to swallow. This sensation continued for some hours. I could not observe an aromatic taste as described by GRESHOFF, which may be accounted for by the fact that he used the root.

GRESHOFF states [1]) that a case of suicide by means of *toeba* has been reported to him in which vomiting and dizziness manifested themselves. Therefore the following experiments were made: A cat was given a large quantity of derrid per os through a stomach-tube. Within 20 minutes vomiting and diarrhoea manifested themselves, followed by disturbances of the equilibrium, with violent dyspnoea. In the beginning all reflexes were present.

There was stimulation of the pilomotores: the hair of back and tail stood on end, as with asphyxia; however the mucous membranes were a bright red, so that this was not a case of asphyxia. The pupils were dilated maximally. After a short time the animal suffered itself to be put in all positions; it showed strong saliva-secretion and perspiration on the foot-soles. The animal lay on the table quite motionless, as if unconscious; the respiration was quickened and deepened, the pulse reduced to half its rate.

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[1]) GRESHOFF. Med XXIX Batavia. 1900 blz. 175.

Gradually all symptoms disappeared till at last only incoordinate walking remained which at length disappeared as well. After three hours the animal looked quite normal again.

With a following experiment a ligature was put round the pylorus-part of the stomach; when the animal had quite recovered from the narcosis it was given, per os, a quantity of derrid equal to that of the previous experiment; after 3 hours no symptoms could be observed. Now the ligature was removed in narcosis, so that the quantity of derrid that was left could get into the intestine. When the animal had recovered from this narcosis, we saw the derrid-symptoms manifest themselves: licking of the mouth, diarrhoea, vomiting, strong secretion of saliva; for the rest of the day it sat quite motionless, with drooping head. Afterwards it quite recovered.

In a third experiment the same ligature was made, and moreover, past this ligature, enterostomia was performed in the first part of the duodenum; an india-rubber tube protruded from the abdomen. When the animal had recovered from the narcosis, a quantity of derrid, equal to that of the previous experiments, was poured through the tube (of course it could not get into the stomach). Now 10 min. after the injection derrid-symptoms manifested themselves: licking of the mouth; violent vomitive movements, during which a slimy substance was removed; diarrhoea; disturbances of the equilibrium; lying on the back; dyspnoea; decreased reflexes, apparent unconsciousness. After a few hours the animal recovered, till at last all symptoms vanished. The intestine was put in its original condition again.

So here we observe the same things as during the other experiments: effect on the central nervous system, respiration and circulation; especially manifest are coordination-disturbances, vomiting, diarrhoea and symptoms coming from the sympathetic nervous system: pupil-dilatation, intensified secretion of saliva and perspiration, besides stimulation of the pilomotores.

Local effect of derrid.

After subcutaneous injections in frogs, white mice, rabbits and guinea-pigs we never saw any reaction manifest itself in the place of injection. Only in frogs a change could be observed in the muscles, which presented itself as a white colouring of the muscle in question; the muscle looked as if boiled and was not electrically sensitive any more. So the local effect may be termed very slight.

Effect on intact animals.

Frogs were subcutaneously injected with derrid (0,5—6 m.g.); "normal animals" were given corresponding quantities of alcohol. Temporariae and esculentae did not show any change. After an injection of 3 m.g. nothing particular could be observed; all reflexes were present, while on stimulation of the spinal cord the legs were put out when a certain position of the secondary coil was reached; heart-and respiration-movements were clearly visible. After 3 hours an animal could stand supination; the head-reflex when the whole frog was horizontally turned round, had disappeared; the sensitiveness of the legs was still present; the position of the secondary coil, on stimulation of the spinal cord, was still the same; the motion of the heart was clearly visible, but respiration-movements could no longer be observed. After 6 hours the sensitiveness had disappeared; after 9 hours heart-movements could be observed no more. The autopsy showed that the heart was in half-systole, which was not always the case. If a muscle-nerve preparation was made, it appeared that nerve and muscles were still sensitive; only in the place of injection the muscle was not sensitive and looked as if boiled. This could not be put down to alcoholic action, which appeared from experiments of comparison. In other experiments defective jumping and other coordination-disturbances could be observed.

From these and other experiments it appears that first brain-narcosis and paralysis of the respiratory-centre manifest themselves; then at last heart-paralysis. In all these cases the electrical sensitiveness of the spinal cord, the motor nerves and muscles remained unchanged till the last (except in the place of injection).

White mice, subcutaneously injected with 0,01—3 mg. did not show reaction until dosed with 0,1 mg., from which they recovered. Action of alcohol was excluded.

A mouse, injected with 0,5 m.g. reacted after $1^1/_2$ hours on touching the cornea and pinching its tail; respiration visible; heart-beat could be felt; after $3^1/_2$ hours the rate of the respiration had considerably lowered; rate of the pulse unchanged; after 5 hours it could stand being put in all positions, reacted upon pinching its tail and its legs; after 8 hours no signs of life could be observed; during the autopsy muscular movements showed themselves and the heart was still beating; the latter showed the changes previously mentioned. In other cases we saw a kind of catalepsy: when put with two legs on the edge of a table it remained sitting, while its other legs were hanging over the edge and its tail was held quite straight.

So here as well we see narcosis of the higher centres, paralysis of the respiratory-centre, and at last of the heart; moreover coordination-disturbances.

Rabbits, intravenously injected, immediately showed disturbances of the equilibrium when sufficiently dosed; the animals rolled on the floor, had violent convulsions, shrieked sometimes and died through paralysis of the respiration.

Artificial respiration brought the animals back to life again, as stated before. A guinea-pig also showed action on the centre, followed by death. Animals can also be poisoned per os, as appears from the experiments on cats.

After all these experiments I give the following summary:

Derrid is a poison having no strong local effect; it causes a peculiar sensation on the mucous membranes of mouth and lips; it causes no changes on the conjunctiva; administered per os, subcutaneously or intravenously, it brings about violent symptoms of poisoning, beginning with vomiting and diarrhoea, followed by an effect on the central nervous system, with disturbances in the coordination of the movements, decreasing of sensitiveness, deepening of respiration and then stoppage of the breath. The poison also acts on the sympathetic nervous system, which appears from dilatation of the pupils, increased secretion of saliva and perspiration and stimulation of the pilomotores.

In larger doses it also acts upon the heart, while irregularities and slowing of the pulse manifest themselves, besides falling of the bloodpressure, followed by heart-paralysis.

As to its place in the pharmacological system, derrid cannot be included in any of the existing groups. It does not belong to the saponins, as strong local effect and laking-power are wanting; neither does it belong to the narcotics, for the decrease of sensitiveness quite retreats into the background compared with the other symptoms; nor can it be included in the digitalis-group, because its action on the circulation apparatus does not justify this.

So for this poison which, as is apparent from preliminary experiments, has the same effects as some other drugs, a new group must be formed, the "group of the derrid-drugs".

It would seem to me that as yet little is to be expected from derrid, therapeutically.

Physics. — "*On* NERNST'S *theorem of heat.*" By Prof. PH. KOHNSTAMM and Dr. L. S. ORNSTEIN. (Communicated by Prof. J. D. VAN DER WAALS.)

1. Recently Dr. F. E. C. SCHEFFER drew attention in an address[1]) to NERNST'S "theorem of heat". This "theorem of heat" consists in the "supposition" that at the absolute zero the quantities A and E i.e. the maximum work and the change of energy for a chemical reaction in a condensed system would not only be equal, but would also have the same differential quotient with respect to temperature. It is not said explicitly that in the differentiation the volume is supposed constant, but it may be assumed that this is meant. This theorem of heat enables us, to express the constant of integration of VAN 'T HOFF'S equation:

$$\frac{dln\,K}{dT}=\frac{q}{RT^2}$$

in the constant of integration of CLAPEYRON'S equation applied to the saturate vapour:

$$\frac{T\,dp}{p\,dT}=\frac{\lambda}{RT},$$

in which for λ is chosen an empirical expansion into a series. In this way NERNST finds that the constant of integration of VAN 'T HOFF'S equation, C, (when the K is expressed in partial pressures), is in connection with the constant of integration of the vapour pressure, c, according to the equation:

$$C=\Sigma\nu c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which ν is the number of molecular quantities of every substance, which take part in the reaction, and the Σ sign is to be extended over all the substances, the disappearing substances being counted negative.

By the aid of suppositions about the specific heats which we need not discuss here, and of the experimental data of the vapour pressure lines NERNST determines the value of c for a number of substances from the formula for their vapour pressure line found by the empirical expansion into series for λ. It now appears that for some of these substances this c has about the same value, namely about 1.1 f, in which f is the factor from VAN DER WAALS' well-known empirical vapour pressure formula. This enables him to find a value of c also for substances whose vapour pressure line is not

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[1]) See Chemisch Weekblad 1910, N°. 43.

accurately known, and then the C and so the K is calculated with the values found in this way from equation (1) for a number of reactions. These values sometimes harmonize remarkably well with those found experimentally.

2. This agreement is really so close that it can hardly be ascribed to "chance". On the other hand the most serious objections rise to the reasoning on which the calculation is based. For the maximum work A is nothing but the difference in free energy before and after the reaction $A = \psi_1 - \psi_2$: in the same way $E = \varepsilon_2 - \varepsilon_2$, and accordingly these quantities are connected through the equation:

$$A - E = T\left(\frac{\partial A}{\partial T}\right)_v$$

or, in GIBBS's terminology:

$$(\psi_2 - \psi_1) - (\varepsilon_2 - \varepsilon_1) = - T\,(\eta_2 - \eta_1).$$

So NERNST's "theorem of heat" states that at the absolute zero not only the second member becomes zero for condensed systems, but also its differential quotient with respect to T for constant volume, i.e.:

$$\eta_2 - \eta_1 + T\left(\frac{\partial\,(\eta_2 - \eta_1)}{\partial T}\right)_v = 0\,. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now for a temperature T and a volume v so great that we may consider the contents as a rarefied gas, the entropy of a mixture of n components, of which resp. $\mathbf{r}_2\ \mathbf{r}_2\ \mathbf{r}_n$ molecular quantities are present is

$$\eta_1 = \Sigma \mathbf{r}\, MR \log v + \int_1^T \frac{\Sigma \mathbf{r} c_{v\infty}}{T}\, dT + \Sigma \mathbf{r} H + \Sigma R \mathbf{r} \log \mathbf{r}$$

in which H is the constant of entropy for every substance at the temperature 1 and the volume 1. The latter must be supposed so great that the gas laws are applicable.

If this mixture is compressed to a volume v_1, the entropy will amount to:

$$\eta_1 = \int_1^{v_1} \left(\frac{\partial p}{\partial T}\right)_v dv + \int_1^T \frac{\Sigma \mathbf{r} c_{1\infty}}{T}\, dT + \Sigma \mathbf{r}\, H + \Sigma R \mathbf{r} \log \mathbf{r} \quad . \quad (3)$$

We cannot determine the value of the first integral, until the equation of state of the mixture is known. We shall, therefore, begin by putting an imaginary case, chosen as simple as possible, and demonstrate that at least for this case the "theorem of heat" cannot apply. And this not so much because we consider this case in itself as decisive against the theorem of heat (for we should first have to show that such a case really occurs in nature), but because this case leads us into the very heart of the question, and thus will enable us to get rid of the restricting suppositions from which we started. For the case in question we choose a reaction between a number of substances, which takes place without modification of the total number of molecules, and for which VAN DER WAALS' equation in its simplest form with constant a and b may be taken as equation of state both of the mixture of the reacting substances, and of the reaction products.

In this case the entropy of the mixture of the reacting substances is given by

$$\eta_{\varepsilon_1} = (\Sigma \mathbf{r} MR) \log (v_1 - b_1) + \int_1^T \frac{\Sigma \mathbf{r} c_{1v\infty}}{T} dT + \Sigma \mathbf{r} H + \Sigma R \mathbf{r} \log \mathbf{r}$$

and that of the reaction products:

$$\eta_{\varepsilon_2} = (\Sigma \mathbf{r} MR) \log (v_2 - b_2) + \int_1^T \frac{\Sigma \mathbf{r} c_{v_2\infty}}{T} dT + \Sigma \mathbf{r} H + \Sigma R \mathbf{r} \log \mathbf{r}$$

So we get for the difference of entropy:

$$\eta_{\varepsilon_2} - \eta_{\varepsilon_1} = \Sigma \mathbf{r} MR \log (v_2 - b_2) - \Sigma \mathbf{r} MR \log (v_1 - b_1) +$$

$$+ \int^T \frac{\Sigma \mathbf{r} c_{2v\infty}}{T} dT - \int^T \frac{\Sigma \mathbf{r} c_{1v\infty}}{T} dT + \Sigma \mathbf{r} H + \Sigma \mathbf{r} \log \mathbf{r}$$

3. What value now does this expression assume at the absolute zero? It is clear that no general answer is to be given to this, because this value will depend on the way in which we approach the absolute zero. For as for $T = 0$ necessarily always v must

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[1] It is true that strictly speaking we should have to reason as follows. The value $\varepsilon_2 - \varepsilon_1$ for the considered reaction is put equal by NERNST to the difference of energy in the formula of VAN 'T HOFF, and the latter applies to reactions for constant volume; so the volume before and after the reaction is kept constant. But except in the highly improbable case that exactly $b_2 = b_1$, one of the two volumes, (that of the mixture with the smallest b), does not become equal to the limiting volume. And this leads to obvious absurdity, both because then one of the two systems is necessarily unstable, and because of the conclusions which we should then further have to draw from the equality of the differential quotients. If we are to attach any meaning to NERNST's suppositions, we shall have to assume, as has been tacitly done in the text, that according to NERNST's meaning the substances are under the pressure of their saturate vapour before and after the reaction, and that for the substitution in the equation of VAN 'T HOFF we may neglect the difference of volume, which in consequence of this necessarily accompanies the reaction. This conception alone can account for the way mentioned in the text in which NERNST determines the maximum work (by evaporation and condensation without further operations with the condensed system).

become $=b$[1]), we have here a number of terms which approach infinity, but independent of each other. Only when we indicate exactly in what way we make v approach to b with decrease of temperature, we can find a definite value for $\eta_2 - \eta_1$, and only then the question put makes sense.

The way in which NERNST determines the maximum work, makes it impossible for him to see this. He makes all the reacting substances evaporate reversibly, then the reaction take place, and at last the reaction products condense reversibly. Everywhere he neglects the volumes of the condensed phase by the side of that of the gas phase. But as has already been observed by Dr. SCHEFFER, this is not allowed here, because the great terms cancel each other, and accordingly the difference of entropy will depend on the relation of the volumes in the condensed system.

Therefore it does not appear, of course, from NERNST's papers what way of approach is exactly meant in the "theorem of heat", but as is demonstrated more fully in the footnote, on p. 702, it is impossible to assume anything else than that the approach to the absolute zero is meant in such a way that the substances before and after the reaction are under the pressure of their saturate vapour, or in other words that we reach the point $T=0$, $v=b$ along the border line both for the reacting substances and for the reaction products.

4. Then the result will depend on the way in which the volumes along the border line depend on the temperature. If we assume that $v_1 - b_1 = \alpha_1 f(T)$ and $v_2 - b_2 = \alpha_2 f(T)$, the sum of the first two terms becomes finite, and that of the last two infinite, because in general the specific heats of the reaction products and of the reacting substances are certainly not the same for gas mixtures. $\left(\frac{\partial(\eta_2 - \eta_1)}{\partial T}\right)_v$ takes a finite value, viz. the difference of the specific heats, and so the expression (2) does not become zero, but infinite. We can only evade this conclusion by making such a hypothesis about the dependence of $v_2 - b_2$ and $v_1 - b_1$ on the temperature, that this infinity just disappears, i. e. by putting:

$$v_1 - b_1 - \alpha_1 T^{\frac{\Sigma \nu c_{1v}}{\Sigma \nu MR}} f(T) \text{ and } v_2 - b_2 = \alpha_2 T^{\frac{\Sigma \nu c_{2v}}{\Sigma \nu RM}} f(T)$$

Apart from the fact that this brings us in collision with the law of the corresponding states[1]), which must certainly hold in this case,

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[1]) For in corresponding states the c_v do not become equal. Comp. VAN DER WAALS—KOHNSTAMM Lehrbuch der Thermodynamik p. 66.

the theorem of heat is not fulfilled yet, for then we get in the neighbourhood of $T=0$:

$$\eta_2 - \eta_1 = \Sigma \nu \, MR \log \frac{c_2}{c_1} + \Sigma \nu H + \Sigma R\nu \log \nu \quad (4)$$

So $\left(\frac{\partial(\eta_2-\eta_1)}{\partial T}\right)_v$ for $T=0$, and a fortiori $T\left(\frac{\partial(\eta_2-\eta_1)}{\partial T}\right)_v$ become zero, and the theorem of heat further imposes the condition, that the expression (4) becomes zero, or that:

$$\Sigma \nu H = \Sigma \nu \, MR \log \frac{c_1}{c_2} + \Sigma R\nu \log \nu \quad . \quad . \quad . \quad (5)$$

And now it has become clear why we could say above that our result is independent of the special form of the equation of state. For even if we should be willing to accept that the deviations which the real substances show from the simple suppositions made here, have always exactly that value that prevents the difference of entropy (2) from becoming infinite, this difference will never become zero as the theorem of heat requires, unless a relation like (5) is fulfilled.

According to this expression we could calculate the difference of the constants of the entropy of the reacting substances before and after the reaction from quantities which are perfectly determined by the equation of state. If we, however, consider in what way these arbitrary constants of entropy have been introduced into equation (3), this result becomes altogether absurd.

5. It seems to us that this has sufficiently refuted the "theorem of heat" for so far as we have to understand by it the opinion that $\left(\frac{\partial A}{\partial T}\right)_v$ and $\left(\frac{\partial E}{\partial T}\right)_v$ must be equal in the absolute zero. Nor can the conclusion drawn from it, equation (1), be maintained. NERNST himself would probably have seen this, if instead of starting from the differential equation for $\frac{dlnK}{dT}$, which VAN 'T HOFF has given, he had started from the integral relation for lnK, already drawn up by GIBBS in his well-known paper. For then he would have known what the physical meaning is of the constant of integration occurring in his equation (1), viz. that this contains besides the specific heats the constants of entropy of the reacting substances, and so that exactly the same essential objection exists to his equation (1), as we have just advanced against equation (5). But then he would also have seen that if he wanted to calculate the chemical equilibria, he should not put the question: How do the substances behave at the

absolute zero? but that he should have asked: How can I get to know anything about those constants of entropy?

Or in other words: The regularities discovered by NERNST do not prove anything about the absolute zero, much less about the equality of $\left(\frac{\partial A}{\partial T}\right)_v$ and $\left(\frac{\partial E}{\partial T}\right)_v$ in that point, but they show that in the cases examined by NERNST there must exist a certain relation between the constants of entropy of the reacting substances and other quantities characteristic of these substances, in this sense that the difference of the sum of the constants of entropy before and after the reaction can be calculated from quantities which are characteristic of the pure, unmixed substances.

6. Now in what way can we account for the fact that such a relation appears to exist, and of what nature are the quantities characteristic of the pure substances which occur in it? It is clear that we cannot restrict ourselves to purely thermodynamic considerations to answer these questions. For the way in which the entropy is defined in thermodynamics, $d\eta = \frac{dQ}{T}$, naturally implies that the constant of entropy is an indefinite and arbitrary quantity. Only when we succeed in giving another, integral definition of the entropy it is conceivable that we should get a better insight into this constant.

So we have to take recourse to the kinetic methods of BOLTZMANN and GIBBS, by the aid of which integral definitions have really been drawn up for the entropy so that it is possible entirely to determine the quantities defined by them, at least for the rarefied gas state in a definite system of unities. The entropy for a monatomic gas defined according to the method of GIBBS has been calculated by one of us (O) in his thesis for the doctorate p. 56:

$$\eta = \frac{3}{2} n + \frac{3}{2} n \log 2 \pi \theta m + \log v.$$

It is now natural to suppose that the relation discovered by NERNST means that the entropy-constants thus defined are the quantities which determine the value of the constant member of the equation of equilibrium. But on further consideration it appears that this supposition is untenable, at least for so far as it concerns these entropy constants as wholes. Not only because GIBBS's definition, even though one takes the η_{ger} [1]), leads to another constant than BOLTZMANN's H contains, which, moreover, need only be equal to the thermodynamic entropy

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[1]) Cf. POSTMA. These Proc. Oct. 1908, p. 311.

with the exception of an additive constant; what we said appears in a much more conclusive way from this that the values of these constants depend on the system of units used, and that in such a way that with change of these unities new additive constants appear. If e. g. the unit of time is multiplied by c_t, the constant is increased by $n \log c_t$ [1]). On the other hand the values determined by **Nernst** can, evidently, not change by a change of the unit of time [2]); so these values can never be the whole of the entropy constant, however kinetically defined. So we have to divide the constants of entropy of the reacting substances into two parts, one part which remains constant during the reaction, and which finally disappears from the equation of equilibrium, and one part which changes during the reaction. Or to take a concrete example, the constant of entropy of a definite quantity of hydrogen must consist of a part that refers to the atoms H, and which remains constant for the same number of atoms in whatever state they may be before and after the reaction, and of a part which is determined by the configuration in which these atoms are found, and which therefore varies during the reaction. The former part must depend on the unit of time in the way indicated by Gibbs or Boltzmann; but being constant in every chemical reaction, it will necessarily disappear from the difference of entropy before and after the reaction. The latter part, on the other hand, determines the equation of equilibrium, and so can reversely, be found from it. The values found by Nernst, must give us information about this part. What will be the physical meaning of it? The only indication which thermodynamics can give about it, is implied in the observation in note [2]). For when the number of molecules changes, $\log K$ becomes dependent on the unit of volume in this sense that an additive constant $r \log c_e$ appears, in which c_e is the ratio between the old and the new unit, and r the modification of the number of molecular quantities by the reaction. So the difference of entropy must not depend on the unit of volume for a reaction with constant number of molecules, and for another reaction it must be increased by an additive constant on modification of the unit of volume. So it lies at hand to suppose that the quantities characteristic of the difference of entropy must be logarithms of volumes

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[1]) Cf. Gibbs, Principles in statistical mechanics, p. 19. Boltzmann's H depends on the units in another way, but it is also increased by an additive constant if the unit of time is increased and the other units remain constant.

[2]) As $\ln K$ can depend on the unit of volume, when namely the number of molecules changes during the reaction, the values found by Nernst can be subjected to a change when we change the unit of volume.

characteristic of the pure substances. A further confirmation of this supposition and characterisation of these quantities can only be given by a kinetic theory of the chemical phenomena. Such a theory we find already in BOLTZMANN's "Gastheorie" and we shall see that NERNST's results are in principle already implied in it.[1])

7. In this communication we shall restrict ourselves to the kinetic treatment of two simple cases. We shall make use of the statistical method of GIBBS, which easily gives both the conditions of equilibrium and the entropy of a partially dissociated gas.

The first case of dissociation which we consider is one of the type of the dissociation of Iodine vapour ($I_2 \rightleftarrows I + I$).

For this case BOLTZMANN [2]) describes the action of the atoms on each other in the following way. The atoms are supposed to be perfectly rigid, elastic, and smooth spheres of the diameter σ, which have the mass m distributed homogeneously over the volume. The chemical forces are not active in all directions round the atoms, but are restricted to certain regions at the circumference. They have, however, always the direction of the line connecting the centres of the bound atoms. The following may serve to describe the action of the forces somewhat more accurately. Let A (fig. 1) be the centre of an atom; the centre B of a second atom now must lie outside the sphere S_A, which has been described round A with a radius σ. If the second atom is to be bound to the atom A, it is necessary that B lies in a volume ω_A, which is firmly connected with S_A, and adjoins it, while A must lie in the corresponding volume ω_B

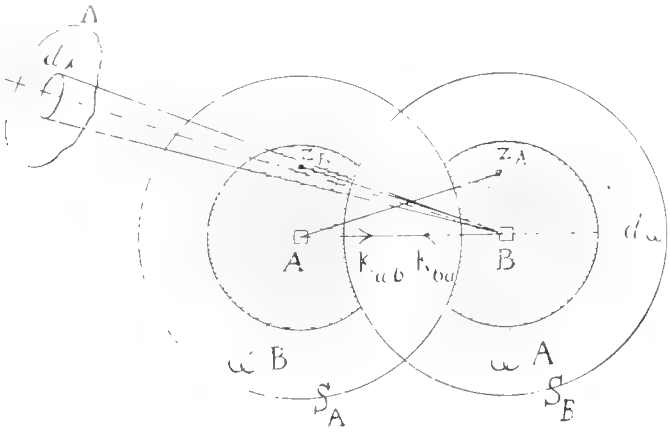

Fig. 1.

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[1]) This is the more remarkable, because NERNST indeed mentions BOLTZMANN's work in his first paper Gött. Nachrichten 1906 p. 7, but adds: "doch haben sich neue praktisch verwendbare Resultate auf diesem Wege bisher nicht ergeben."

[2]) Gastheorie II. p. 177.

adjoining S_B (sphere with radius σ round B). We shall call the line which connects A with the centre of gravity of ω_A the axis of the atom A. (AZ_A).

By making use of the quantities which determine the situation of the axis, we can express the condition on which two atoms are bound somewhat more simply, viz.: Two atoms whose centres are A and B, are bound, if B lies in an element $d\omega$ of the region ω_A, the axis of B lying inside a cone of the opening A. The configuration of the atom B with respect to the atom A is known if we know the element $d\omega$ where its centre lies and the elementary cone $d\lambda$, which contains the direction of the axis of the atom. The forces are always directed along the line connecting the centres; the mutual energy of the chemical attraction $-\chi_{11}$ does not depend on the angles which determine the direction of the axes. If BZ_B lies outside A, $\chi_{11} = 0$. On this supposition the chemical forces have no influence on the rotations of the molecules round axes through the centre, nor have the forces occurring in a collision (compare the suppositions of page 707.[1]) So the kinetic energy of the rotations mentioned is invariable, we shall put it zero.

8. We now consider a canonic ensemble of the modulus Θ, which is built up of systems, in which n atoms of the described kind are found in a volume V. Now we shall inquire into the number of the systems in this ensemble, in which n_1 atoms are free, and $2n_2$ atoms bound to n_2 molecules. We shall, however, apply the simplification that the density of the considered system is so small that we may ignore the size of the molecules when determining the said number. First of all we shall note down the number ζ' of the systems in which n_1 definite atoms are free, and $2n_2$ definite atoms are bound to molecules in a definite combination.

We denote the coordinates of the centres by $x_1 \ldots z_n$, the conic elements in which their axes lie by $d\lambda_1 \ldots d\lambda_n$. The potential energy depends exclusively on the coordinates $x_1 \ldots z_n$, the kinetic energy being determined by the corresponding moments. According to GIBBS's definition the number ζ'' of the systems, in which the mentioned moments have all possible values, but the coordinates lie between x_1 and $x_1 + dx_1 \ldots z_n$ and $z_n + dz_n$, the interval $d\lambda_1 \ldots d\lambda_n$ being left for the axes, is given by:

$$\zeta'' = N e^{\frac{\Psi}{\Theta}} (2\pi\Theta m)^{\frac{3}{2}n} e^{-\frac{\varepsilon}{\Theta}} dx_1 \ldots dz_n \, d\lambda_1 \ldots d\lambda_n.$$

---

[1] If we put that ω_A lies entirely within S_B, only one atom can be bound with A in the sphere ω_A by the forces at the same time.

Ψ is a constant corresponding with the free energy, ε represents the potential energy, which is here only chemical energy, as we shall leave VAN DER WAALS' attraction forces out of consideration.

Now to find ζ' we must sum ζ'' with respect to the coordinates and conic openings for all cases in which n_1 atoms are free and the others bound to definite pairs. On account of the applied simplification the coordinates of the n_1 free atoms and of n_2 of the bound atoms can traverse the whole volume V, the available space for $d\lambda$ for each of them amounting to 4π. If we calculate this sum we find for the contribution of all the considered systems to the number ζ':

$$N e^{\frac{\Psi}{\Theta}} (2\pi\,\Theta m)^{\frac{3}{2}n} (4\pi V)^{n_1+n_2} e^{-\frac{\varepsilon}{\Theta}} dx_{n_1+n_2+1} \ldots dz_n \, d\lambda_{n_1+n_2+1} \ldots d\lambda_n$$

Then the remaining n_2 atoms must be placed so that they are bound to those of the n_2 atoms which have been pointed out; if we take all the configurations into account for which this is the case, we see easily that:

$$\zeta' = N e^{\frac{\Psi}{\Theta}} (2\pi\,\Theta m)^{\frac{3}{2}n} (4\pi)^n V^{n_1+n_2} \left\{ \int \frac{d\lambda\, d\omega}{4\pi} e^{\frac{\chi_{11}}{\Theta}} \right\}^{n_2}$$

is found for ζ'.

For constant $d\omega$ the integral in the second member must be extended over A (p. 708), while further we must ascribe all positions of the region ω to $d\omega$. We shall denote this integral by k_{11}. As χ_{11} and Θ have the dimension of an energy, k_{11} has that of a volume.

9. To find the total number of the systems that contain n_1 free atoms and n_2 molecules, we must consider that from n atoms groups of n_1 and $2n_2$ atoms can be formed in

$$\frac{n!}{n_1!\,(2n_2)!}$$

ways, and that further the $2n_2$ atoms can be joined to pairs in

$$(2n_2-1) \ldots 5 \,.\, 3 \,.\, 1 = \frac{(2n_2)!}{2^{n_2} n_2!}$$

ways.

So the total number of the considered systems in the ensemble amounts to:

$$\zeta = N e^{\frac{\Psi}{\Theta}} (2\pi\,\Theta\, m)^{\frac{3}{2}n} \frac{n!}{n_1!\, n_2!\, 2^{n_2}} (4\pi)^n V^{n_1+n_2} k_{11}^{n_2},$$

where $n_1 + 2n_2 = n$. This number will be maximum, when:

$$\delta \log \zeta = 0$$

if

$$dn_1 + 2dn_2 = 0.$$

As the condition on which ζ is maximum we find .

$$\frac{2n_2}{n_1^2} = \frac{k_{11}}{V}.$$

Moreover

$$-\frac{1}{n_1}\,dn_1^2 - \frac{1}{n_2}\,dn_2^2 < 0$$

which is identically satisfied. So the "true" state of equilibrium for a dissociated gas is stable.

10. To calculate Ψ we have only to consider that $\Sigma\zeta$ taken for all possible values of n_1 and n_2 yields the total number of the systems of the ensemble, that is N. We shall further understand by n_1 and n_2 the numbers of free atoms and molecules in the state of equilibrium; we can then denote a deviating state by the expressions $n_1 - 2\tau$ and $n_2 + \tau$. The number of the systems deviating in this way is then;

$$\zeta_\tau = \frac{Ne^{\frac{\Psi}{\Theta}}\,(2\pi\Theta m)^{\frac{3}{2}n}\,(4\pi n)^n\,V^{n_1+n_2}\,e^{-n_2}\,k_{11}^{\,n_2}}{n_1^{\,n_1}\,n_2^{\,n_2}}\sqrt{\frac{2\pi n}{2\pi n_1\;2\pi n_2}}\;e^{-\tau^2\frac{n+2n_2}{n_1\,2n_2}}$$

Here $n!$ has been developed according to the formula of STIRLING. If we put n_2 small with respect to n we find by summing with respect to τ from $-\infty$ to $+\infty$:

$$N = \frac{Ne^{\frac{\Psi}{\Theta}}\,(2\pi\Theta m)^{\frac{3}{2}n}\,(4\pi n)^n\;V^{n_1+n_2}\,e^{-n_2}\,k_{11}^{\,n_2}}{n_1^{\,n_1}\,n_2^{\,n_2}}.$$

Also when n_2 is not small with respect to n the sum yields a factor of the order of unity, which is without influence on the value of Ψ; strictly speaking the limits for τ are $-n_2$ and $n - n_2$; but we may take $-\infty$ and $+\infty$ for them, because for somewhat high values of τ very small amounts are found.

So we have for Ψ:

$$-\frac{\Psi}{\Theta} = n\,log\,4\pi n + \frac{3}{2}\,n\,log\,(2\pi\Theta m) + (n_1 + n_2)\,log\,V +$$
$$+ n_2\,log\,k_{11} - n_1\,log\,n_1 - n_2\,log\,n_2 - n_2\,log\,2 - n_2.$$

From this follows for the pressure of the dissociated gas:

$$\frac{p}{\Theta} = \frac{n_1 + n_2}{V} + (log\,V + log\,k_{11} - log\,n_2 - log\,2 - 2)\,\frac{\partial n_2}{\partial V} +$$
$$+ (log\,V - log\,n_1 - 1)\,\frac{\partial n_1}{\partial V}$$

By the aid of the condition of equilibrium and the condition $n_2 + 2n_2 = 0$, we easily see that the sum of the two last terms is 0, so that we find:

$$\frac{p}{\Theta} = \frac{n_1 + n_2}{V}.$$

Now we introduce the special supposition that χ_{11} is the same for the whole region ω; then we have:

$$k_{11} = \int \frac{d\lambda}{4\pi}\, d\omega\, e^{\frac{\chi_{11}}{\Theta}} = e^{\frac{\chi_{11}}{\Theta}} \int \frac{d\lambda}{4\pi}\, d\omega = e^{\frac{\chi_{11}}{\Theta}}\, w_{11}.$$

We shall call w_{11}, which represents a volume, the reduced volume of the chemical region of attraction, or shorter the chemical volume of the atom.

Now we find for Ψ:

$$-\frac{\Psi}{\Theta} = n \log 4\pi n + \frac{3}{2} n \log (2\pi \Theta m) + (n_1 + n_2) \log V -$$

$$- n_1 \log n_1 - n_2 \log n_2 - n_2 - n_2 \log 2 + \frac{n_2 \chi_{11}}{\Theta} + n_2 \log w_{11}.$$

On an average the kinetic energy for the ensemble amounts to $\frac{3}{2} n\Theta$; so the potential energy, which is equal to that of the most frequently occurring system amounts to $- n_2\chi_{11}$: hence the statistical entropy $\eta = \frac{\varepsilon - \Psi}{\Theta}$ is given by:

$$\bar{\eta} = \frac{3}{2} n + n \log 4\pi n + \frac{3}{2} n \log (2\pi \Theta m) + (n_1 + n_2) \log V -$$

$$- n_1 \log n_1 - n_2 \log n_2 - n_2 \log 2 - n_2 + n_2 \log w_{11},$$

a formula which yields the desired generalisation of the cited formula for the case under consideration.

11. In this communication we shall now still briefly treat the case of the dissociation of the type:

$$2HI \rightleftarrows I_2 + H_2$$

$$I_2 \rightleftarrows I + I$$

$$H_2 \rightleftarrows H + H$$

Concerning the action of the chemical forces we make analogous suppositions. The action of I on I, and of H on H, as well as that of I on H is described by the aid of regions of attraction ω_{11}, ω_{22}, and ω_{12}, the mutual potential energy, which is again assumed to be independent of the direction of the axes characterized by the conic elements $d\lambda_{11}$, $d\lambda_{22}$, and $d\lambda_{12}$, being denoted by $-\chi_{11}$, χ_{22}, and χ_{12}. The following integrals are represented by k_{11}, k_{22}, and k_{12}

$$\int \frac{d\lambda_{11}}{4\pi}\, d\omega_{11}\, e^{\frac{\chi_{11}}{\Theta}} = k_{11}\,,$$

$$\int \frac{d\lambda_{22}}{4\pi}\, d\omega_{22}\, e^{\frac{\chi_{22}}{\Theta}} = k_{22}\,,$$

$$\int \frac{d\lambda_{12}}{4\pi}\, d\omega_{12}\, e^{\frac{\chi_{12}}{\Theta}} = k_{12}.$$

Let us now again consider a canonic ensemble of the modulus Θ, built up of a system, in which n_1 atoms I, and n_2 atoms H, are found in the volume V. Arguing in an analogous way to the preceding case we now see easily that the number of the systems in which n_{10} definite I atoms are free, $2n_{11}$ definite I atoms are bound to definite pairs, n_{12} definite I atoms are bound with definite H atoms, $2n_{22}$ definite H atoms are bound to pairs, and n_{20} H atoms are free amounts to ζ':

$$\zeta' = N e^{\frac{\Psi}{\Theta}} (2\pi\Theta m_1)^{\frac{3}{2}n_1} (2\pi\Theta m_2)^{\frac{3}{2}n_2} (4\pi)^{n_1+n_2} V^{n_1+n_2-n_{11}-n_{22}-n_{12}} k_{11}{}^{n_{11}} k_{22}{}^{n_{22}} k_{12}{}^{n_{12}},$$

in which m_1 and m_2 represent the mass of a I, and of an H atom.

As from n_1 atoms I and n_2 atoms H groups of $2n_{11}$ etc. atoms can be formed in:

$$\frac{n_1!}{(2n_{11})!\, n_{10}!\, n_{12}!} \text{ resp. } \frac{n_2!}{2n_{22}!\, n_{20}!\, n_{12}!}$$

ways, and the $2n_{11}$ atoms I and $2n_{22}$ atoms H can be combined to pairs in resp.:

$$\frac{(2n_{11})!}{2^{n_{11}}\, n_{11}!} \text{ and } \frac{(2n_{22})!}{2^{n_{22}} n_{22}!}$$

ways, while n_{12} molecules HI can be formed from the chosen numbers H and I in $n_{12}!$ ways, we find for the number of considered systems in the ensemble:

$$\zeta = N e^{\frac{\Psi}{\Theta}} (2\pi\Theta m_1)^{\frac{3}{2}n_1} (2\pi\Theta m_2)^{\frac{3}{2}n_2} (4\pi)^{n_1\;\;n_2} V^{n_{10}+n_{11}+n_{12}+n_{22}+n_{20}}$$
$$\frac{n_1!\, n_2!}{n_{10}!\, n_{11}!\, n_{12}!\, n_{22}!\, n_{20}!\, 2^{n_{11}} 2^{n_{22}}}\, k_{11}{}^{n_{11}}\, k_{22}{}^{n_{22}}\, k_{12}{}^{n_{12}}.$$

We must now examine on what conditions ζ is maximum, if the following equations hold:

$$n_1 = n_{10} + 2n_{11} + n_{12}$$
$$n_2 = n_{20} + 2n_{22} + n_{12}\,.$$

For these conditions we find:

$$\frac{2n_{11}}{n_{10}^2} = \frac{k_{11}}{V},$$
$$\frac{2n_{22}}{n_{20}^2} = \frac{k_{22}}{V},$$
$$\frac{k_{11}k_{22}}{k_{12}^2} = \frac{4n_{11}n_{22}}{n_{12}^2}.$$

which accordingly supplies a sufficient number of equations with the two mentioned conditions. If we put the quantities χ equal over the whole region ω, we have:

$$k_{11} = e^{\frac{\chi_{11}}{\Theta}}\, w_{11}$$
$$k_{22} = e^{\frac{\chi_{22}}{\Theta}}\, w_{22}$$
$$k_{12} = e^{\frac{\chi_{12}}{\Theta}}\, w_{12}\,.$$

The quantities w_{11}, w_{22}, and w_{12} again have the dimension of a volume. So the conditions of equilibrium are also to be reduced to the form:

$$\frac{e^{\frac{\chi_{11}}{\Theta}}\, w_{11}}{V} = \frac{2n_{11}}{n_{10}^2}$$
$$\frac{e^{\frac{\chi_{22}}{\Theta}}\, w_{22}}{V} = \frac{2n_{22}}{n_{20}^2}$$
$$e^{\frac{-2\chi_{12}+\chi_{11}+\chi_{22}}{\Theta}}\, \frac{w_{11}w_{22}}{w_{12}^2} = \frac{4n_{11}n_{22}}{n_{12}^2} \quad . \; . \; . \; . \; . \; . \; . \quad (6)$$

The quantity $\chi_{22}+\chi_{11}-2\chi_{12}$ represents the change of energy in the reaction $I_2 + H_2 \rightarrow 2HI$.

We find for the free energy:

$$e^{-\frac{\Psi}{\Theta}} = (2\pi\Theta m_1)^{\frac{3}{2}n_1} (2\pi\Theta m_2)^{\frac{3}{2}n_2} (4\pi)^{n_1+n_2} \frac{n_1^{n_1} n_2^{n_2} e^{-n_{11}-n_{12}-n_{22}}}{n_{10}^{n_{10}} n_{11}^{n_{11}} n_{12}^{n_{12}} n_{22}^{n_{22}} n_{20}^{n_{20}} 2^{n_{11}} 2^{n_{22}}}$$
$$V^{n_{10}+n_{11}+n_{12}+n_{22}+n_{20}} k_{11}^{n_{11}} k_{22}^{n_{22}} k_{12}^{n_{12}}.$$

For the pressure:

$$\frac{p}{\Theta} = \frac{n_{10}+n_{11}+n_{12}+n_{22}+n_{20}}{V}.$$

And for the entropy η.

$$
\begin{aligned}
\eta = \frac{3}{2} n_1 + \frac{3}{2} n_2 + \frac{3}{2} n_1 \log (2\pi\Theta m_1) + \frac{3}{2} n_2 \log (2\pi\Theta m_2) \\
+ n_1 \log 4\pi n_1 + n_2 \log 4\pi n_2 \\
- n_{10} \log n_{10} - n_{11} \log n_{11} - n_{12} \log n_{12} - n_{22} \log n_{22} - n_{20} \log n_{20} \\
- n_{11} - n_{12} - n_{22} - n_{11} \log 2 - n_{22} \log 2 \\
+ (n_{10} + n_{11} + n_{12} + n_{22} + n_{20}) \log V \\
+ n_{11} \log w_{11} + n_{22} \log w_{22} + n_{12} \log w_{12} .
\end{aligned}
$$

12. If we now compare equation (6) with GIBBS's thermodynamically derived equation, we find the above supposition (p. 707) quite confirmed. For apart from the variability of the specific heats which we have excluded by our suppositions about the constancy of χ and the character of the bond between the atoms, the two equations agree entirely, only in the thermodynamic equation the indefinite quantity $\Sigma \nu H$ occurs, here $\Sigma \nu \log w$. So the "theorem of heat" reduces to this thesis, which is self-evident on the suppositions of BOLTZMANN, that the "chemical volume" w of a definite chemical substance is a quantity characteristic of this substance, with which it appears in each of the reactions in which it takes part. So it is also these volumes whose size can be determined from the equation of equilibrium. And it is clear from what has been said above (p. 706) that from reactions for which the number of molecules does not change, only relative values of these volumes can be found for different substances. If the number of molecules does change, absolute values can also be calculated for them, as indeed, has already been done by BOLTZMANN [1]).

If we finally ask whether NERNST's numerical calculations have supplied us with new data for the knowledge of the chemical volumes, we dare not answer in the affirmative. First of all it has, namely, already appeared from calculations by Dr. SCHEFFER, that the arbitrariness which remains in the choice of the specific heats is such that even for the most closely examined reactions we can vary the value of $\Sigma \nu H$ within a very wide margin without coming into conflict with the experiments. Therefore it may justly be doubted if not other values than those given by NERNST, would agree with the experimental data. Moreover, however, NERNST's values contain not only the $\Sigma \nu H$, but also the $\Sigma \nu c_v$. So a calculation of the volumes under consideration, which wants to give more than the order of magnitude is possible only when one takes the difference in specific

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[1]) Gastheorie II § 66.

heat of the different substances into account, which has not been done as yet in what precedes.

Finally we will point out that the above remarks also give us an insight into the signification of the theory of the "chemodynamic temperature scale" drawn up by HABER in his: "Thermodynamik technischer Gasreaktionen". HABER is of opinion that for all gas reactions for which the number of molecules does not change, the same unit of temperature is to be given which makes the constant of the equation of equilibrium zero. Because, as we said, both $\Sigma r H$ and $\Sigma r c_v$ occur in this constant, it is now clear that this comes to this that at the temperature $T = 1$ of that scale the same relation would hold for all substances between the size of their "chemical volumes" and their specific heat. A priori little seems to plead in favour of the assumption of such a relation. But here too, it will only be possible to take a decision by the aid of a kinetic theory which accounts for the variability of the specific heats in connection with a very accurate knowledge of the experimental data.

Physiology. — *"Unisegmental reflex-reactions."* By Prof. G. VAN RIJNBERK. (Communicated by Prof. C. WINKLER.)

Both in physiology and in clinical work it is hold to be a fundamental axioma of the theory of reflex-reactions, that as the most simple expression of the reflexive function may be considered a unisegmental or monomere reflex, where the skinfield receiving the stimulus, the afferent nerve-tract, the turning-point in the medulla, the efferent nerve-tract and the muscle (or the gland) performing the reaction are altogether and exclusively seated within one and the same segment of the body and of the medulla.

The course of the influent dorsal nerve-fibres relative to the cells of the dorsal and ventral grey horn (the co-ordinative and the executive system), within one single segment of the medulla, apparently may be assumed to offer a quite sufficient substratum for a monomere reflex. Still, to my knowledge at least, nobody ever had observed such a simple reflex, because in all cases where reflexive reactions were investigated whose inductive and abducent nerve-tracts belonged to the same nerve-root of the medulla and consequently to the same segment of the body, the segment of the medulla serving as turning-point, still retained its connection with a larger tract of the medulla, and was not therefore isolated anatomically nor functionally.

For some time I was occupied by the question, whether a segment of the medulla isolated in this latter way, might wholly independently continue to be capable of reflexive function, and a few years ago I succeeded, basing upon former investigations, to find, as has been related elsewhere [1]), that in the toad (Bufo vulgaris), a small portion of the medulla, encompassing approximatively the irradiating zone of the 2nd nerve-root of the medulla (= 1st nerve of the arm), continues to be capable of provoking reflexive reactions, even when the whole remainder of the central nerve-system had been destroyed.

At present I am enabled to relate the results of investigations made on dogs. These experiments were taken in the following manner.

On a dog, preferably a young one, that had been put into morphia-chloroform-ether-narcosis, the medulla in the thoracal-lumbar region was opened over a length of at least seven segments. Next, without opening the dura meninx, to the right and to the left at least three pairs of nerve-roots were cut through from foreward to backward, one pair of roots was left intact and below this latter, three or more others were cut through on both sides. The wounds in skin and muscle were then provisionally suturated by a few sutures, and the moment was awaited that the animal would be sufficiently awakened from the narcosis to react when the skin was excited by painful stimuli. Then, by means of the usual method (pinching), to the right and to the left on the trunk the skin-fields, that had become analgetic in consequence of nerve-roots having been cut through, were defined as to their situation, their shape and their extension, and likewise the sensible area lying between these former and corresponding to the region innervated by the uninjured root (dermatoma). The boundaries thus found, were traced as usually with a pencil.

After this the dog was once more put into narcosis, the suturating was unfastened and the medulla opened anew, the dura mater of the segment containing the uninjured pair of roots was cut open and the course of the fascicles of nerve-fibres in it carefully observed, after which the medulla was quickly cut through, a little space before the place of entrance of the most cranial fascicle and a little space behind that of the most caudal fascicle, and some warm moistened ganze was put upon the wound in order to prevent hemorrhage. The narcosis was stopped immediately afterwards, and the investigations began to discover what reflexive function might eventually have been retained.

In a series of similar experiments I have found, that whenever

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[1]) Folia Neurobiologica. II. 6. 718—729. Leipzig. 1909.

the isolated segment belonged to those nerve-roots supplying the nether-extremity with sensory and motory nerves, there never was to be traced any vestige of reflexive reaction on stimuli applied to the isolated dermatoma. When on the contrary a segment from the thoracal or lumbar region had been isolated, it remained still possible in most cases to observe some expression of retained reflexive function. After a slight mechanical excitation of the skin on the isolated dermatoma, that had first been proved to have retained sensibility, there followed regularly a short contraction in certain muscles. When either the 13th thoracal or one of the first lumbar segments had been isolated, this contraction was observerd in a more or less sharply defined portion of the M. longissimus dorsi and of the M. ileocostalis. The place where this contraction presented itself, apparently depended on the serial number of the isolated segment. In cases where one of the more cranial thoracal segments had been isolated, there appeared, besides the contraction of the M. longissimus dorsi, still another contraction in the intercostal muscles of the same segment by means of which two ribs were moved towards one another.

These reflexive muscle-contractions were easiest to be provoked by an exceedingly gentle mechanical stimulus, applied to a portion of the skin-surface not too strictly defined, f. i. by stroking the wrong way with a finger-tip the hairs that had been cut short. Nevertheless the stimulus, in whatever manner applied, seemed to be effective only when applied within the dorsal region of the dermatoma.

In one case only, after exciting the ventral region of *LI*, contractions appeared in a portion of the m. obliquus abdominis, situated nearly under the isolated dermatoma.

These symptoms of reflexive reactions appeared with still more clearness, whenever I employed the method for increasing reflexive reactions by means of a strictly local application of a solution of strychnine-salts on the dorsal surface of the medulla, a method [1]) elaborated by my assistent-doctor Mr. DUSSER DE BARENNE. If f.i. nitrate of strychnine in a solution of 1$^0/_0$ was applied to the isolated segment of the medulla, the excitability to reflexive reactions of the segment was notably increased. After the gentlest mechanical touch there followed then in the muscles named before a contraction much more evident and intense. Moreover, on exciting the skin-field on one side, apparently with the same intensity there ensued a contraction in the symmetrical muscles of the other half of the body, the expression of a crossed reflex.

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[1]) Compare Folia Neurologica V. 1, 42—58. Haarlem 1911.

The symptoms described in the foregoing, may be observed in all cases, provided the operations of the vertebral column and of the medulla are made with the necessary precautions. It result that, to all appearance, in mammals too, every single segment of the medulla, at any rate in the thoracal and upper lumbar region, is capable of performing the reflexive function separately and independent from the remainder of the central nerve-system.

Chemistry. "*On the three isomeric fluorobenzenes and some of their derivatives.*" By Prof. A. F. HOLLEMAN and J. M. SLOTHOUWER.

(Communicated in the meeting of October 29, 1910).

This communication will not appear in these Proceedings.

(January 26, 1911).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday January 28, 1911.

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E. H. BÜCHNER: "Investigations on the radium content of rocks". II. (Communicated by Prof. A. F. HOLLEMAN), p. 818.

P. VAN ROMBURGH: "On the action of nitrous acid on dinitrodialkylanilines", p. 820.

A. SMITS and H. L. DE LEEUW: "Confirmations of the new theory of the phenomenon of allotropy". I. (Communicated by Prof. J. D. VAN DER WAALS), p. 822. (With one plate).

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Crystallography. — *"On the orientation of microscopic crystal-sections."* By J. Schmutzer. (Communicated by Prof. C. E. A. Wichmann).

(Communicated in the meeting of December 24, 1910).

If in a slide a crystal shows the traces of three non-parallel planes it is possible to determine the orientation of the section without making use of the extinction angle. If the optic constants of an anisotropic mineral are known, it is sufficient to know the extinction angle and the apparent angle between two planes (crystal, cleavage- or twinning-planes) as will be more distinctly demonstrated in a subsequent communication.

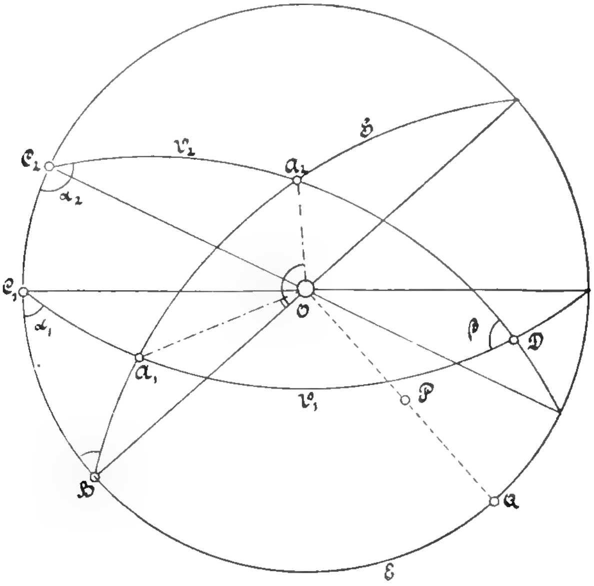

Fig 1.

In fig. 1 the crystal planes E, V_1, and V_2, the former of which is supposed to be the projection plane, are cut by the secant plane S, producing with it the secants OB, OA_1, and OA_2. In stead of the two angles α_1 and α_2 one measures in the secant plane, consequently in the slide, between the planes $V_1 : E$ and $V_2 : E$ the apparent angles $A_1OB = h_1$ and $A_2OB = h_2$.

Be the secant-plane S given by its pole P_1, of which the height $PQ = a$ is measured > 0 above and < 0 below the equator plane, whilst the azimuth $C_1BQ = \varrho$ is > 0 if measured in opposite direction to the hands of a clock, then is in $\angle BA_1C_1$:

$$\cot A_1B = \frac{\sin A_1BC_1 \cot A_1C_1B + \cos A_1BC_1 \cos BC_1}{\sin BC_1}$$

$$-\cot h_1 = \frac{\sin (90-\sigma) \cot \alpha_1 + \cos (90-\sigma) \cos (\varrho-90)}{\sin (\varrho-90)}$$

or

$$\cot h_1 \cos \varrho = \cos \sigma \cot \alpha_1 + \sin \sigma \sin \varrho \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Now is $\smile C'_1C'_2 = \gamma$ a constant that can be calculated with the help of the given angles α_1, α_2 and β from $\angle C'_1C'_2D$ and that is measured from C_1 positively in a direction opposite to the hands of a clock. In $\angle BA_2C_2$ is then:

$$\cot A_2B = \frac{\sin A_2BC_2 \cot A_2C_2B + \cos A_2BC_2 \cos BC_2}{\sin BC_2}$$

$$-\cot h_2 = \frac{\sin (90-\sigma) \cot \alpha_2 + \cos (90-\sigma) \cos (\varrho-90-\gamma)}{\sin (\varrho-90-\gamma)}$$

$$-\cot h_2 = \frac{\cos \sigma \cot \alpha_2 + \sin \sigma \sin (\varrho-\gamma)}{-\cos (\varrho-\gamma)}$$

$$\cot h_2 (\cos \varrho \cos \gamma + \sin \varrho \sin \gamma) = \cos \sigma \cot \alpha_2 + \sin \sigma \sin (\varrho-\gamma)$$

$$\cot h_2 \cos \varrho \cos \gamma = \cos \sigma \cot \alpha_2 + \sin \sigma \sin (\varrho-\gamma) - \cot h_2 \sin \varrho \sin \gamma \quad . \quad . \quad (2)$$

If one divides (2) by (1), then becomes

$$\cot h_2 \cos \gamma (\cos \sigma \cot \alpha_1 + \sin \sigma \sin \varrho) =$$
$$= \cot h_1 \{\cos \sigma \cot \alpha_2 + \sin \sigma \sin (\varrho-\gamma) - \cot h_2 \sin \varrho \sin \gamma\}.$$

$$\cos \sigma (\cot \alpha_1 \cot h_2 \cos \gamma - \cot \alpha_2 \cot h_1) + \sin \sigma \{\sin \varrho (\cot h_2 - \cot h_1) \cos \gamma +$$
$$+ \cot h_1 \cos \varrho \sin \gamma\} + \cot h_1 \cot h_2 \sin \varrho \sin \gamma = 0.$$

If one supposes

$$\left.\begin{array}{l} \cot \alpha_1 \cot h_2 \cos \gamma - \cot \alpha_2 \cot h_1 = a \\ (\cot h_2 - \cot h_1) \cos \gamma = b \\ \cot h_1 \sin \gamma = c \\ \cot h_1 \cot h_2 \sin \gamma = d \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

then the formula changes into

$$a \cos \sigma + \sin \sigma (b \sin \varrho + c \cos \varrho) + d \sin \varrho = 0$$

$$\cos \sigma = -\frac{b \sin \varrho + c \cos \varrho}{a} \sin \sigma - \frac{d}{a} \sin \varrho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If one substitutes this value of $\cos \sigma$ in (1), one obtains:

$$a \cot h_1 \cos \varrho = -\cot \alpha_1 \{(b \sin \varrho + c \cos \varrho) \sin \sigma + d \sin \varrho\} + a \sin \sigma \sin \varrho =$$
$$= \sin \sigma \{-(b \sin \varrho + c \cos \varrho) \cot \alpha_1 + a \sin \varrho\} - d \cot \alpha_1 \sin \varrho$$

from which follows:

$$\sin \sigma = \frac{a \cot h_1 \cos \varrho + d \cot \alpha_1 \sin \varrho}{(a - b \cot \alpha_1) \sin \varrho - c \cot \alpha_1 \sin \varrho}.$$

When worked out this formula furnishes:

$$\sin \sigma = - \frac{a \cos \varrho + \cot \alpha_1 \cot h_2 \sin \gamma \sin \varrho}{\cot \alpha_1 \sin \gamma \cos \varrho + (\cot \alpha_2 - \cot \alpha_1 \cos \gamma) \cos \varrho}.$$

If one supposes herein again

$$\left.\begin{array}{l} \cot \alpha_1 \cot h_2 \sin \gamma = e \\ \cot \alpha_2 - \cot \alpha_1 \cos \gamma = f \\ \cot \alpha_1 \sin \gamma = g \end{array}\right\} \quad \ldots \ldots \ldots \quad (5)$$

then becomes

$$\sin \sigma = - \frac{a \cos \varrho + e \sin \varrho}{g \cos \varrho + f \sin \varrho} \quad \ldots \ldots \ldots \quad (6)$$

We found above

$$\cos \sigma = - \frac{b \sin \varrho + c \cos \varrho}{a} \sin \sigma - \frac{d}{a} \sin \varrho$$

$$\cos \sigma = \left(\frac{b \sin \varrho + c \cos \varrho}{a} \right) \left(\frac{a \cos \varrho + e \sin \varrho}{g \cos \varrho + f \sin \varrho} \right) - \frac{d}{a} \sin \varrho =$$

$$= \frac{(b \sin \varrho + c \cos \varrho)(a \cos \varrho + e \sin \varrho) - d (g \cos \varrho + f \sin \varrho) \sin \varrho}{a (g \cos \varrho + f \sin \varrho)} =$$

$$= \frac{\sin^2 \varrho (eb - fd) + \sin \varrho \cos \varrho (ab + ec - gd) + ac \cos^2 \varrho}{a (g \cos \varrho + f \sin \varrho)} =$$

$$= \frac{h \sin^2 \varrho + b \sin \varrho \cos \varrho + c \cos^2 \varrho}{g \cos \varrho + f \sin \varrho} \quad \ldots \ldots \ldots \ldots \quad (7)$$

in which

$$h = \cot h_2 \sin \gamma \quad \ldots \ldots \ldots \ldots \quad (8)$$

The variables ϱ and σ are consequently separated: the ratio

$$\sin^2 \sigma + \cos^2 \sigma = 1$$

furnishes

$$(a \cos \varrho + e \sin \varrho)^2 + (h \sin^2 \varrho + b \sin \varrho \cos \varrho + c \cos^2 \varrho)^2 = (g \cos \varrho + f \sin \varrho)^2$$

$$\cos^2 \varrho (a^2 - g^2) + 2 \sin \varrho \cos \varrho (ae - fg) + \sin^2 \varrho (e^2 - f^2) +$$
$$+ (h \sin^2 \varrho + b \sin \varrho \cos \varrho + c \cos^2 \varrho)^2 = 0.$$

If one introduces:

$$\cos^2 \varrho = \frac{1 + \cos 2\varrho}{2}; \quad \sin^2 \varrho = \frac{1 - \cos 2\varrho}{2}; \quad 2 \sin \varrho \cos \varrho = \sin 2\varrho,$$

the latter ratio changes into:

$$\cos^2 2\varrho \{(c-h)^2 - b^2\} + 2 \cos 2\varrho (a^2 + c^2 + f^2 - e^2 - g^2 - h^2) +$$
$$+ \{b^2 + (h + c)^2 + 2(a^2 + e^2 - g^2 - f^2)\} +$$
$$+ 2 \sin 2\varrho \{2(ae - fg) + b (h + c) + b (c - h) \cos 2\varrho\} = 0$$

If one supposes

$$\left.\begin{aligned}\frac{2(a^2+c^2+f'^2-e^2-g^2-h^2)}{(c-h)^2-b^2}&=p\\ \frac{b^2+(h+c)^2-2(a^2+e^2-g^2-f'^2)}{(c-h)^2-b^2}&=q\\ \frac{4(ae-fg)+2b(h+c)}{(c-h)^2-b^2}&=r\\ \frac{2b(c-h)}{(c-h)^2-b^2}&=s\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

then becomes

$$cos^2 2\varrho + p\,cos\,2\varrho + q = -(r + s\,cos\,2\varrho)\,sin\,2\varrho \quad . \quad . \quad . \quad (10)$$

and

$$cos^4\,2\varrho + \frac{2(p-rs)}{1+s^2}\,cos^3\,2\varrho + \frac{p^2+2q+r^2-s^2}{1+s^2}\,cos^2\,2\varrho +$$
$$+ \frac{2(pq-rs)}{1+s^2}\,cos\,2\varrho + \frac{q^2-r^2}{1+s^2} = 0 \quad . \quad . \quad . \quad (11)$$

This equation can now be solved: the value found for ϱ, introduced into (6) furnishes σ.

If however in the equation (6)

$$a\,cos\,\varrho + e\,sin\,\varrho = g\,cos\,\varrho + f\,sin\,\varrho = 0,$$

then $sin\,\sigma$ becomes indefinite. In that case is

$$tg\,\varrho = -\frac{a}{e} = -\frac{g}{f}$$

$$af = eg$$

consequently

$$(cot\,\alpha_1\,cot\,h_2\,cos\,\gamma - cot\,\alpha_2\,cot\,h_1)\,(cot\,\alpha_2 - cot\,\alpha_1\,cos\,\gamma) =$$
$$= cot^2\alpha_1\,cot\,h_2\,sin^2\,\gamma = cot^2\,\alpha_1\,cot\,h_2\,(1-cos^2\gamma)$$

$$cot\,\alpha_1\,cot\,h_2\,(cot\,\alpha_2\,cos\,\gamma - cot\,\alpha_1) + cot\,\alpha_2\,cot\,h_1\,(cot\,\alpha_1\,cos\,\gamma - cot\,\alpha_2) = 0$$

$$\frac{cot\,\alpha_1\,cot\,h_2}{cot\,\alpha_2\,cot\,h_1} = \frac{cot\,\alpha_1\,cos\,\gamma - cot\,\alpha_2}{cot\,\alpha_1 - cot\,\alpha_2\,cos\,\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

σ is then found by introducing the value of ϱ in (1).

What is said here finds an application to the determination of the plane that cuts the octahedron planes $(1\bar{1}1)$, (111) and $(\bar{1}11)$ in such a way that the traces of the planes $(1\bar{1}1):(111)$ and $(\bar{1}11):(111)$ enclose right angles. If one supposes (111) to be the equator plane, then becomes

$\alpha_1 = 180° - 70°31'43'', \{V_1 = (1\bar{1}1)\}$; $\alpha_2 = 70°31'43'', \{V_2 = (\bar{1}11)\}$; $\gamma = -60°$; $h_1 = h_2 = 90°$; $\varrho = -30°$.

The equation (12) changes into $0 = 0$; in (6) not only the numerator becomes $= 0$ because $a = e = 0$; but also the denominator because

$$\begin{aligned} & g \cos \varrho + f \sin \varrho = \\ & = \cot \alpha_1 \sin \gamma \cos \varrho + (\cot \alpha_2 - \cot \alpha_1 \cos \gamma) \sin \varrho = \\ & = \cot \alpha_1 \{\sin \gamma \cos \varrho - (1 + \cos \gamma) \sin \varrho\} = \\ & = \cot \alpha_1 \left\{ - \sin^2 60^\circ + \left(1 + \frac{1}{2}\right) \sin 30^\circ \right\} = \\ & = \cot \alpha_1 \left(- \left(\frac{1}{2} \sqrt{3}\right)^2 + \frac{3}{2} \cdot \frac{1}{2} \right) = 0 \end{aligned}$$

From (1) one finds on the contrary

$$\cot h_1 \cos \varrho = 0 = \cos \sigma \cot \alpha_1 + \sin \sigma \sin \varrho$$

$$tg\, \sigma = - \frac{\cot \alpha_1}{\sin \varrho} = - \frac{\cot 70^\circ 31' 43''}{\sin 30^\circ}$$

from which $\sigma = - 35^\circ 15' 53''$, the angle between $(001):(111) - \frac{\pi}{2}$.

The secant plane is consequently (001).

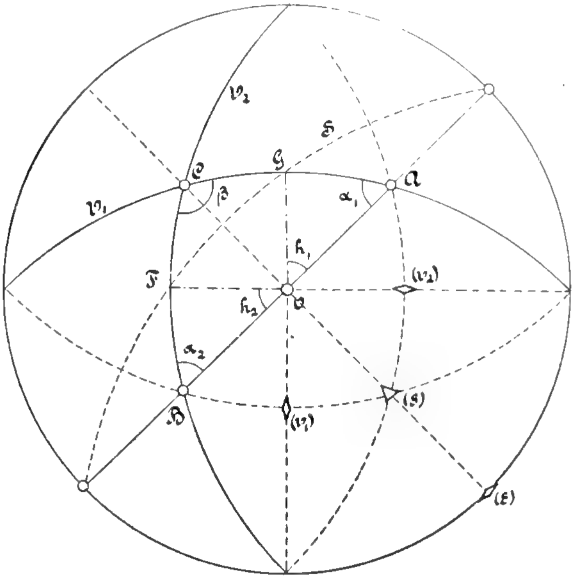

Fig. 2.

A single example may suffice to demonstrate the applicability of the formulas deducted above; I choose for it a problem in which the result obtained can easily be controlled.

The three rhombododecahedron planes (101), (110) and (011) are cut by a plane in such a way, that their traces include angles of 60°. What is the orientation of the secant-plane?

Take E (110) as equator plane; $V_1 : E = \alpha_1 = -60^\circ$; $V_2 : E = \alpha_2 = 60^\circ$; $h_1 = \angle GOA = 60^\circ$; $h_2 = \angle FOB = -60^\circ$;

$$\gamma = \frown AB = (\bar{1}11) : (\bar{1}11) = \quad 109^\circ 28' 17''.$$

$$cot\ \alpha_1 = -cot\ \alpha_2 = -cot\ h_1 = cot\ h_2 .$$

So according to (3), (5) and (8):

$$\begin{array}{ll} a = cot^2\ \alpha_1\ (cos\ \gamma - 1) & e = cot^2\ \alpha_1\ sin\ \gamma \\ b = 2\ cot\ \alpha_1\ cos\ \gamma & f = -\ cot\ \alpha_1\ (1 + cos\ \gamma) \\ c = -\ cot\ \alpha_1\ sin\ \gamma & g = cot\ \alpha_1\ sin\ \gamma \\ d = -\ cot^2\ \alpha_1\ sin\ \gamma & h = cot\ \alpha_1\ sin\ \gamma. \end{array}$$

Here is

$$cot\ \alpha_1 = -\frac{1}{3}\sqrt{3} \quad ; \ cot^2\ \alpha_1 = \frac{1}{3}$$

$$cos\ \gamma = -\frac{1}{3} \quad ; \ sin\ \gamma = -\frac{2}{3}\sqrt{2}.$$

so that (9):

$$p = \frac{2(a^2 + c^2 + f^2 - e^2 - g^2 - h^2)}{(e-h)^2 - b^2} = -\frac{2}{21}$$

$$q = \frac{b^2 + (h+c)^2 + 2\ (a^2 + e^2 - g^2 - f^2)}{(e-h)^2 - b^2} = -\frac{1}{7}$$

$$r = 2\ \frac{2(ae - fg) + b(h+c)}{(e-h)^2 - b^2} = -\frac{4}{21}\sqrt{2}$$

$$s = \frac{2b\ (e-h)}{(e-h)^2 - b^2} = -\frac{4}{7}\sqrt{2}$$

further is in equation 11 :

$$l = \frac{2\ (p + rs)}{1 + s^2} = \frac{4}{27} = \frac{4}{3^3}$$

$$m = \frac{p^2 + 2q + r^2 - s^2}{1 + s^2} = -\frac{14}{27} = -\frac{14}{3^3}$$

$$n = \frac{2\ (pq - rs)}{1 + s^2} = -\frac{20}{81} = -\frac{20}{3^4}$$

$$o = \frac{q^2 - r^2}{1 + s^2} = -\frac{23}{729} = -\frac{23}{3^6}.$$

Consequently we have to solve the equation:

$$cos^4\ 2\varrho + \frac{4}{3^3}\ cos^3\ 2\varrho - \frac{14}{3^3}\ cos^2\ 2\varrho - \frac{20}{3^4}\ cos\ 2\varrho - \frac{23}{3^6} = 0 \quad . \quad (13)$$

Suppose $cos\ 2\varrho = x - \frac{1}{4}\,l = x - \frac{1}{3^3}$, then (13) can be changed into:

$$x^4 + \lambda x^2 + \mu x + \nu = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

in which

$$\lambda = m - \frac{3}{8} l^2 = - \frac{2^7}{3^5}$$

$$\mu = n - \frac{1}{2} lm + \frac{1}{8} l^3 = - \frac{2^{12}}{3^9}$$

$$\mathrm{r} = o - \frac{1}{4} ln + \frac{1}{16} l^2 m - \frac{3}{256} l^4 = - \frac{2^{12}}{3^{11}}$$

If one composes now the equation

$$y^3 + a' y^2 + b' y + c' = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

in which

$$a' = \frac{\lambda}{2} = - \frac{2^6}{3^5}$$

$$b' = \frac{\lambda^2 - 4\mathrm{r}}{16} = \frac{2^{12}}{3^{11}}$$

$$c' = - \frac{\mu^2}{64} = - \frac{2^{18}}{3^{18}}$$

then the roots of (14) are given by:

$$x_{1.2.3.4} = \pm \sqrt{y_1} \pm \sqrt{y_2} \pm \sqrt{y_3},$$

in which

$$\sqrt{y_1}\,\sqrt{y_2}\,\sqrt{y_3} = - \frac{\mu}{8} = \frac{2^9}{3^9} > 0.$$

In order to solve (15) one supposes $y = z - \frac{1}{3} a'$, by which the equation changes into:

$$z^3 + rz + w = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

In this is

$$r = b' - \frac{1}{3} a'^2 = \frac{2^{12}}{3^{11}} - \frac{1}{3} \left(\frac{2^6}{3^5} \right)^2 = 0$$

$$w = c' - \frac{1}{3} a'b' + \frac{2}{27} a'^3 = - \frac{2^{18}}{3^{18}} + \frac{1}{3} \cdot \frac{2^6.2^{12}}{3^5.3^{11}} - \frac{2}{3^3} \cdot \frac{2.^{18}}{3^{15}} =$$

$$= \frac{- 2^{18} + 3.2^{18} - 2.2^{18}}{3^{18}} = 0.$$

(16) furnishes consequently 3 equal roots $z = 0$.

(15) furnishes 3 equal roots $y = z - \frac{1}{3} a' = \frac{2^6}{3^6}$.

To (14) correspond the values

$$x_1 = + \sqrt{y} + \sqrt{y} + \sqrt{y} = 3 \sqrt{y} = \frac{2^3}{3^2}$$

$$x_2 = \sqrt{y} - \sqrt{y} - \sqrt{y} = - \sqrt{y} = - \frac{2^3}{3^3}.$$

The roots of (13) are consequently represented by :

$$\cos 2\varrho_1 = x_1 - \frac{1}{3^3} = \frac{2^3}{3^2} - \frac{1}{3^3} = \frac{23}{3^3}$$

$$2\varrho_1 = \pm 31°35'8'' ; \quad \varrho_1 = \pm 15°47'34''$$

$$\cos 2\varrho_2 = x_2 - \frac{1}{3^3} = -\frac{2^3}{3^3} - \frac{1}{3^3} = -\frac{1}{3}$$

$$2\varrho_2 = \pm 109°28'16'' ; \quad \varrho_2 = \pm 54°44'8''.$$

The corresponding values of σ are calculated from (6) :

$$\sin \sigma = -\frac{a \cos \varrho + e \sin \varrho}{g \cos \varrho + f \sin \varrho} = -\frac{\cot^2 \alpha_1 (\cos \gamma - 1) \cos \varrho + \cot^2 \alpha_1 \sin \gamma \sin \varrho}{\cot \alpha_1 \sin \gamma \cos \varrho - \cot \alpha_1 (1 + \cos \gamma) \sin \varrho} =$$

$$= -\cot \alpha_1 \frac{(\cos \gamma - 1) \cos \varrho + \sin \gamma \sin \varrho}{\sin \gamma \cos \varrho - (1 + \cos \gamma) \sin \varrho} = -\cot \alpha_1 \frac{-\frac{4}{3} \cos \varrho - \frac{2}{3} \sqrt{2} \sin \varrho}{-\frac{2}{3} \sqrt{2} \cos \varrho - \frac{2}{3} \sin \varrho} =$$

$$= -\cot \alpha_1 \cdot \frac{2 \cos \varrho + \sin \varrho \,.\, \sqrt{2}}{\sqrt{2} \,.\, \cos \varrho + \sin \varrho} = -\cot \alpha_1 \,.\, \sqrt{2} \,. = \frac{1}{3} \sqrt{6} \quad . \quad . \quad . \qquad (17)$$

in which however the term $\sin \varrho + \sqrt{2} \,.\, \cos \varrho$ disappears in the numerator as well as in the denominator.

From

$$\sin \varrho + \sqrt{2} \,.\, \cos \varrho = 0$$

one finds

$$tg\, \varrho = -\sqrt{2},$$

to which corresponds

$$\varrho = -54°44'8'' \text{ (or } 180° - 54°44'8'')$$

and this is one of the two values ϱ_2. Whilst from (17) results the value $\sigma = + 54°44'8''$ (or $180° - 54°44'8''$) the value of σ corresponding to $\varrho = -54°44'8''$ must be calculated from (1).

$$\cot h_1 = \frac{\cos \sigma \cot \alpha_1 + \sin \sigma \sin \varrho}{\cos \varrho}$$

$$\frac{1}{3} \sqrt{3} = \frac{-\frac{1}{3} \sqrt{3} \cos \sigma - \frac{1}{3} \sqrt{6} \sin \sigma}{\frac{1}{3} \sqrt{3}}$$

$$\frac{1}{3} \sqrt{3} = -\cos \sigma - \sqrt{2} \sin \sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (18)$$

$$\cos^2 \sigma + \frac{2}{3} \sqrt{3} \cos \sigma + \frac{1}{3} = 2 (1 - \cos^2 \sigma)$$

$$\cos^2 \sigma + \frac{2}{9} \sqrt{3} \cos \sigma - \frac{5}{9} = 0$$

$$\cos\sigma = -\frac{1}{9}\sqrt{3} \pm \sqrt{\frac{3.15}{81}} = -\frac{1}{9}\sqrt{3} \pm \frac{4}{9}\sqrt{3} = +\frac{1}{3}\sqrt{3} \text{ or } -\frac{5}{9}\sqrt{3}.$$

To $\cos\sigma = \frac{1}{3}\sqrt{3}$ corresponds

$$\varrho = \pm 54°44'8''$$

of these two values only $\sigma = -54°44'8''$ cooresponds to (18). A further investigation shows that the pole of the secant plane S is represented by

$$\varrho = -54°44'8'', \quad \sigma = -54°44'8''.$$

whereas the other values of ϱ and σ do not correspond. The secant plane is the octahedronplane (111) as appears clearly from fig. 2; σ corresponds to the angle between (001) : (111) the cosinus of which is represented by

$$\cos\theta = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2}\sqrt{h_2^2 + k_2^2 + l_2^2}} = \frac{1}{\sqrt{3}} = \frac{1}{3}\sqrt{3}.$$

If the planes E, V_1 and V_2 (vide fig. 1) lie in one zone the formulas (10) and (6) obtain a much less complicate form. Because $\gamma = 0$ the coefficients (3), (5) and (8) change into

$$\left.\begin{aligned} a &= \cot\alpha_1 \cot h_2 - \cot\alpha_2 \cot h_1 \\ b &= \cot h_2 - \cot h_1 \\ f &= \cot\alpha_2 - \cot\alpha_1 \\ c = d &= e = g = h = 0 \end{aligned}\right\} \quad \ldots\ldots \quad (19)$$

so that:

$$\cos^2 2\varrho - \frac{2(a^2 + f^2)}{b^2}\cos 2\varrho - \frac{b^2 + 2(a^2 - f^2)}{b^2} = 0 \quad \ldots \quad (20)$$

$$\sin\sigma = -\frac{a}{f}\cot\varrho \quad \ldots\ldots\ldots \quad (21)$$

In an amphibole crystal the planes $(1\bar{1}0)$, (110) and (010) are lying in one zone; (110) may serve as equator plane. Whilst the real angles between $(\bar{1}10)$: (110) and (010) : (110) are resp. $\alpha_1 = 55°50'$ and $\alpha_2 = -62°5'$ the apparent angles, measured in a rock slide, amounted to $h_1 = 43°$ and $h_2 = -79°$.

(19) gives:

$$a = 0{,}43625 \quad ; \quad a^2 = 0{,}19032$$
$$b = -1{,}26674 \quad ; \quad b^2 = 1{,}60454$$
$$f = -1{,}20858 \quad ; \quad f^2 = 1{,}46070$$

from which:

$$\frac{a^2 + f^2}{b^2} = 1{,}02875 \quad ; \quad \frac{b^2 + 2(a^2 - f^2)}{b^2} = -0{,}58074$$

consequently:

$$\cos^2 2\varrho - 2(1,02875)\cos 2\varrho + 0,58074 = 0$$

$$\cos 2\varrho = 1,02875 \pm \sqrt{(1,02875)^2 - 0,58074} =$$

$$= 1,02875 \pm 0,68948 = 1,71823 \text{ or } 0,33927.$$

Only the second value corresponds, so that:

$$2\varrho = 70°10' \text{ or } -70°10'$$

$$\varrho = 35°5' \text{ or } -35°5' \,.$$

$$\sin\sigma = -\frac{a}{f}\cot\varrho = -\frac{0,43625}{-1,20858}\cot\varrho = 0,36096\cot\varrho$$

from which

$$\varrho_1 = 35°5' \,,\ \sigma_1 = 30°55'$$

$$\varrho_2 = -35°5' \,,\ \sigma_2 = -30°55'.$$

As will appear afterwards the optic extinction offers an expedient to decide in a given case whether one has to do with the secant plane $(\varrho_1\sigma_1)$ or with $(\varrho_2\sigma_2)$.

In a graphical way the problem of the orientation of crystal-sections can be solved in a considerably simpler way. To do so one can make use of diagrams, that give for any discretional angle between two planes, the apparent angle h as a function of ϱ and σ.

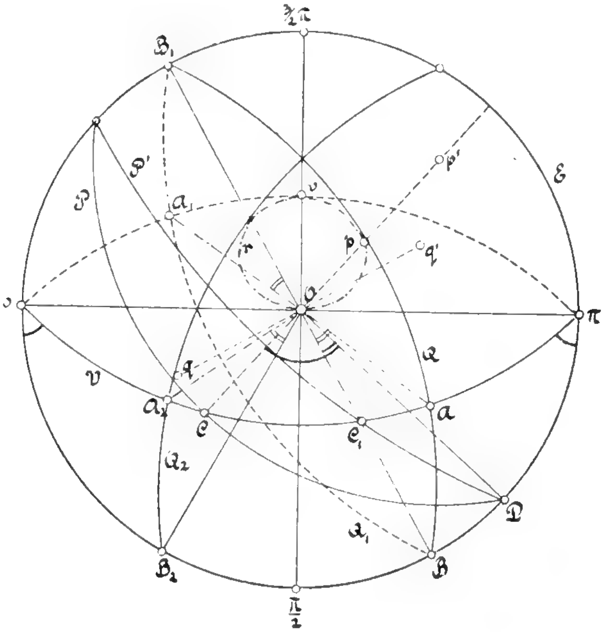

Fig. 3.

In fig. 3 be E again the projection plane, V the crystalplane, that with E includes an angle α, (0) O (π) the secant line between E and V; the azimuth of a secant plane (P, Q) be measured from (0) positively opposite to the direction of the hands of a clock. If one indicates the globe octants (0) $\left(\frac{\pi}{2}\right)$, $\left(\frac{\pi}{2}\right)$ (π), (π) $\left(\frac{3}{2}\pi\right)$ and $\left(\frac{3}{2}\pi\right)$ (0) respectively by the numbers 1, 2, 3, and 4, in so far as they lie above the equatorplane, by 5, 6, 7, and 8 in so far as they lie below it, then one can deduct from the figure with regard to the sign of h in the various octants what follows.

If $0 < \alpha < \frac{\pi}{2}$, and if the pole q of the secant plane Q lies in the first octant, h becomes $= \angle AOB > 0$. In the opposite 7th octant one finds for the secant plane (q', Q') a negative apparent angle; if Q and Q' coincide, so that the distance of the poles is $q : q' = \pi$, then h_1 becomes $= - h$.

If the pole of the secantplane lies in the 2nd octant, then h becomes < 0; if one applies Q_2 with regard to the plane $O\left(\frac{\pi}{2}\right)$ symmetrically with Q then h_2 becomes again $= \angle A_2OB_2 = - h (\angle AOB)$. If at last the pole lies in the plane $O\left(\frac{\pi}{2}\right)$, then $h = 0$ independently of the value of σ.

In the octants 3 and 4 the pole of the secant plane moves exclusively within the obtuse angle $E : V$. If with a constant value of ϱ, we substitute for the pole (p) of the plane (P) successively all the values of σ between 0 and $\frac{\pi}{2}$, it appears that for $\sigma = 0$, $h = 0$; if σ becomes > 0, as in the plane ($p' P''$), h becomes $= \angle C_1OD < 0$; this negative angle becomes larger if σ increases till the pole lies in p, and h has become $= \angle COD = - \frac{\pi}{2}$. Now the negative angle surpasses the value $- \frac{\pi}{2}$ and is consequently measured positively as far as $O\left(h < \frac{\pi}{2}\right)$.

By construction the point p can easily be found, because $\frown Cp = \frac{\pi}{2}$. From (1) follows, that here

$$\cot h \cos \varrho = 0 = \cos \sigma \cot \alpha + \sin \sigma \sin \varrho$$

$$tg\,\sigma = -\frac{cot\,\alpha}{sin\,\varrho}.$$

From this ratio the course of the curve rpO can be deducted, which is the locus of all poles of secant planes that cut the angle between the planes $V:E$ in a way so as to produce the apparent angle $h=\frac{\pi}{2}$. For $\varrho=\pi$ one finds $\sigma=\frac{\pi}{2}$; $\varrho=\frac{3}{2}\pi$ produces $tg\,\sigma = cot\,\alpha$, or $\sigma=\frac{\pi}{2}-\alpha$; whilst for $\varrho=2\pi$, σ becomes again $\frac{\pi}{2}$.

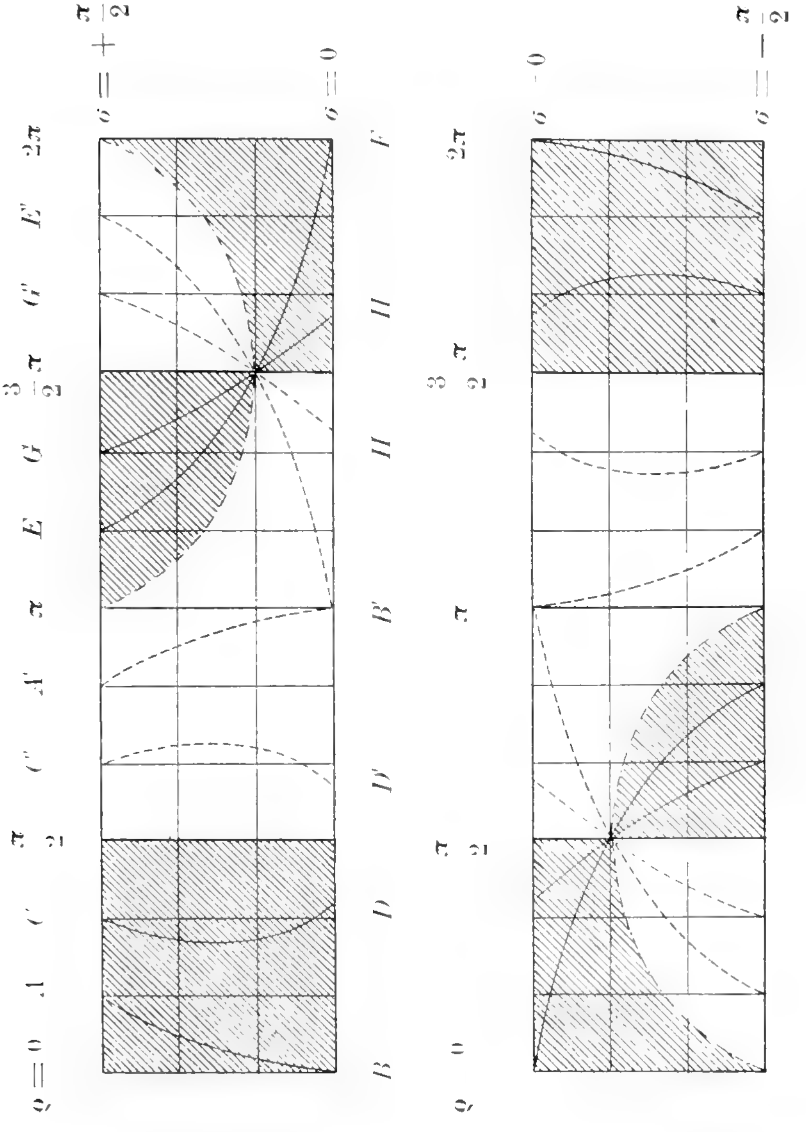

Fig. 4 and 5.

It is easy to see that the areas $O(\pi)\left(\frac{3}{2}\pi\right)rpO$ and Orr furnish a negative, $O(0)\left(\frac{3}{2}\pi\right)vrO$ and Orp on the contrary furnish a positive value for h. For the octants 5 and 6 we find the same as for 3 and 4, only h takes here the opposite sign.

In the figures 4 and 5 one finds the scheme of the h-diagram for $\alpha = 60^\circ$ with the area-division discussed here; the secant planes the poles of which lie in the shadowed areas, form a positive angle h, the white areas form a negative angle. The squares into which the figures are divided, are 30° by 30°; the meridiancircles, on which σ is measured out, are drawn as parallel lines, so that a line equal in length to the equator takes the place of the pole Q. In fig. 4 the octants 1—4, in fig. 5 the octants 5—8 are represented.

In the first octant the curve AB indicates the locus of the poles of all the secant planes that produce $h = 60^\circ$; the curve CD gives $h = 30^\circ$; symmetrically with regard to the line $\left(\varrho = \frac{\pi}{2}\right)\left(\sigma = \frac{\pi}{2}\right) \cdot \left(\varrho = \frac{\pi}{2}\right)\left(\sigma = 0\right)$, to which corresponds $h = 0$ lie in the 2nd octant the curves $C''D'$ with $h = -30^\circ$ and $A'B'$ with $h = \quad 60^\circ$.

If for $\varrho = \pi$, σ varies from 0° to $\frac{\pi}{2}$, then h takes successively all values from -60° to -90°; here the curve Opr of fig. 3 begins going over the point $\left(\varrho = \frac{3}{2}\pi, \sigma = \frac{\pi}{2} - \alpha = 30^\circ\right)$ to $\left(\varrho = 2\pi, \sigma = \frac{\pi}{2}\right)$. The curves EF and GH produce here again values $h = 60^\circ$ and $h = 30^\circ$, the curves $G'H'$ and $E'B'$ respectively 30° and $\quad 60^\circ$.

The diagram for $-\frac{\pi}{2} < \sigma < 0^\circ$ needs no further elucidation; it plainly expresses the above-mentioned identity of the angle h for planes with poles $+\varrho, \pm\sigma$ and $-\varrho, \mp\sigma$. Consequently the octants 1 : 2, 3 : 4, 5 : 6, 7 : 8 are but for the sign symmetrical with regard to the plane $\left(\frac{\pi}{2}\right) : \left(\frac{3}{2}\pi\right)$, cf. fig. 3, whilst the octantpairs (1,2) : (7,8) and (5,6) : (3,4) are symmetrical, but for the sign of σ with regard to the plane $(0) : (\pi)$.

As appears further from fig. 3 the diagram for $\alpha = 60^\circ$ is the same as for $\alpha = -60^\circ$, if one substitutes for ϱ the value $\varrho \pm \pi$, and consequently changes the octant pairs (1,2) and (7,8) resp. for (3,4) and (5,6).

The diagrams of which I have served myself for the graphical solution of the problems discussed above, and which will be published elsewhere, give for angles α varying between 0 and $\pm\frac{\pi}{2}$ and progressing with 10°, the values of h for secant planes, of which azimuth and height of poles, likewise progressing with 10°, vary between $\varrho = 0$ and 2π, $\sigma = 0$ and $\pm\frac{\pi}{2}$. By interpolation the value of h for any indifferent secant plane can be found from it for every value of α with sufficient accuracy.

The way in which the problem must be solved may be explained to two of the problems treated analytically above. If one considers fig. I, then it is clear, that by a graphical treatment one can find $\angle A_1OB = h_1$ in the diagram for $\alpha = \alpha_1$ i. e. with $\varrho = \frown C_1BQ_1$, $\sigma = PQ$; in the same way $\angle A_2OB = h_2$ in the diagram for $\alpha = \alpha_2$ with $\varrho_1 = \frown C_2BQ = \varrho - \gamma$ and $\sigma = PQ$.

If on the contrary one wishes to determine from the given angles α_1, h_1, and α_2, h_2 the locus of the secant plane $P(\varrho,\sigma)$, then the diagrams for α_2 and α_1 must be laid on each other, the latter with regard to the former turned over an angle γ, and one must

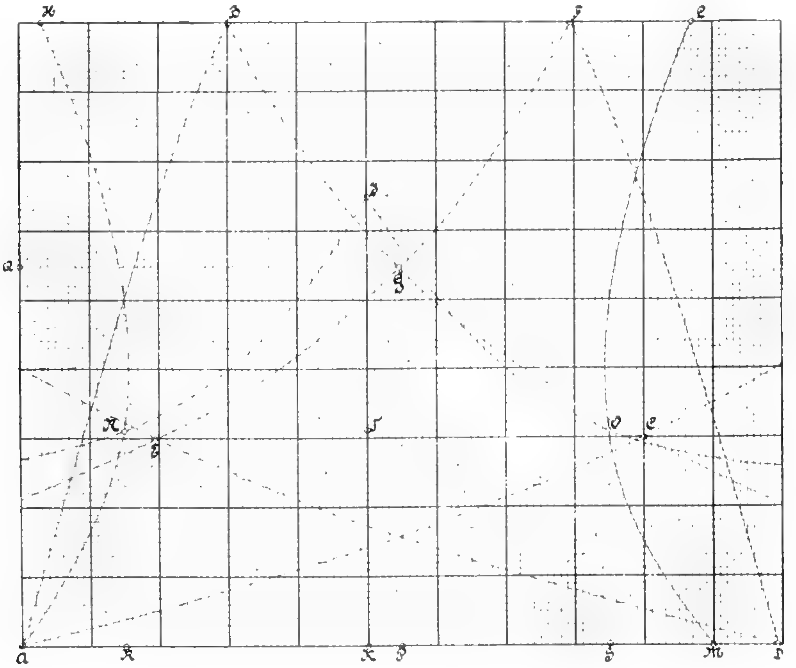

Fig. 6.

see where the curves $h_1(\alpha_1)$ and $h_2\ (\alpha_2)$ meet. The meeting point indicates the pole $P\,(\rho,\sigma)$ of the required secant plane.

In fig. 6 the graphical solution of two of the above discussed problems is represented. If one takes (cf. fig. 2) the rhombododecahedronplane (110) as equatorplane, then the planes (101) and (011) form angles with it equal to $\alpha_1 = -60^\circ$ and $\alpha_2 = 60$. The secant plane S gives $h_1 = 60^\circ$, $h_2 = -60^\circ$; $\gamma = -109^\circ 28' 17''$. If the diagram for α_1 is removed $109^{\circ 1}/_2$ with regard to the diagram for α_2, and both are placed on each other, then it appears, that the curves $h_1\ (60^\circ)$ and $h_2\ (-60^\circ)$ meet only in the 5th octant. In the figure the curves for $\sigma > 0$ and $\sigma < 0$ are drawn side by side. If the azimuth of A is $= 0$, the curve $AB\,(\alpha_2 = 60^\circ)$ indicates the poles for $h_2 = 60^\circ$ with $\sigma > 0$; BC the poles for $h_2 = -60^\circ$ with $\sigma < 0$, AC those for $h_2 = 60^\circ$ with $\sigma < 0$. The azimuth of $D = 109^{\circ 1}/_2$; FD gives the poles for $h_1 =\ \ 60^\circ$ with $\sigma > 0$; FE and DE give those for $h_1 = 60^\circ$ resp. $h_1 = -60^\circ$ with $\sigma < 0$. The meeting point of the curves BC and FE gives the pole of the required secant plane with $\rho = 54^{\circ 3}/_4$ with regard to A, or $\rho = -54^{\circ 3}/_4$ with regard to D, and $\sigma = -54^{\circ 3}/_4$.

The second problem refers to the amphibole-crystal spoken of on page 732, which is cut by the section plane in such a way that the apparent angles between the planes $(\bar{1}10):(110)$ and $(010):(110)$ amount respectively to $h_1 = 43^\circ$ and $h_2 = -79^\circ$.

In fig. 6 the zone-axis $(\rho = 0)$ is indicated by K; the curves LOM and HNA indicate the locus of the poles for $h_1 = 43^\circ$ with $\sigma > 0$ (1st octant) and $\sigma < 0$ (8th octant); the curves IO and IN indicate the locus of the poles for $h_2 = -79^\circ$ with $\sigma > 0$ (1st octant) and $\sigma < 0$ (8th octant). The meeting point of the curves $LM:IO$ and $HA:IN$ gives the points $O\,(\rho = 35^\circ,\ \sigma = 31^\circ)$ and $N\,(\rho = -35^\circ,\ \sigma = -31^\circ)$ which values likewise correspond entirely to those found above in the analytical way.

Mathematics. "*On the Integral equation of* FREDHOLM." By Prof. W. KAPTEYN.

1. Let

$$\varphi(x) = f(x) + \lambda \int^{b} K(xs)\,\varphi(s)\,ds \quad . \quad . \quad . \quad . \quad . \quad (1)$$

be the integral equation of FREDHOLM, in which the constants a, b, λ, and the functions $f(x)$ and $K(xy)$ are known, and $\varphi(x)$ is the function to be determined.

We will suppose that $f(x)$ is continuous in the interval $a < x < b$ and that $K(xy)$ is finite in the square $a \leq x < b$, $a < y \leq b$.

The method of NEUMANN gives then immediately the solution

$$\varphi(x) = f(x) + \lambda \int_a^b \Gamma(x s \lambda) f(s)\, ds$$

where

$$\Gamma(x y \lambda) = K(xy) + \lambda K_2(xy) + \lambda^2 K_3(xy) + \dots \quad (2)$$

and

$$K_n(xy) = \int_a^b K(xs)\, K_{n-1}(sy)\, ds\ .$$

The disadvantage of this solution is that it only converges for certain values of λ. But a much better solution was discovered by FREDHOLM in which the function $\Gamma(x y \lambda)$ is exhibited as the ratio of two power series which are convergent for all values of λ.

Our first object will be to show that the latter solution may be deduced from the former in a very simple way. Supposing that the finite function $K(xy)$ can be expanded in a finite series of the form

$$K(xy) = X_1(x)\, Y_1(y) + X_2(x)\, Y_2(y) + \dots X_n(x)\, Y_n(x) \quad . \quad . \quad (3)$$

it may be shown that a linear relation with constant coefficients exists between $n + 1$ successive functions $K_i(xy)$,

$$\begin{aligned} &\alpha_n K_{p+1}(xy) - \alpha_{n-1} K_{p+2}(xy) + \dots \\ &\qquad + (-1)^{n-1} \alpha_1 K_{p+n}(xy) + (-1)^n K_{p+n+1}(xy) = 0 \quad . \quad . \quad (4) \end{aligned}$$

wherein $p = 0, 1, 2, \dots$ and $K_1(xy) = K(xy)$.

Thus it is evident that the series (2) is a reciprocal one which may be represented as the ratio of two polynomia

$$\Gamma(x y \lambda) = \frac{B_0 - B_1\lambda + B_2\lambda^2 - \dots + (-1)^{n-1} B_{n-1} \lambda^{n-1}}{1 - \alpha_1\lambda + \alpha_2\lambda^2 - \dots + (-1)^n \alpha_n \lambda^n} \quad (5)$$

where

$$\left.\begin{aligned} B_0 &= K_1 \\ B_1 &= \alpha_1 K_1 - K_2 \\ B_2 &= \alpha_2 K_1 - \alpha_1 K_2 + K_3 \\ &\dots\dots\dots \\ B_{n-1} &= \alpha_{n-1} K_1 - \alpha_{n-2} K_2 + \dots + (-1)^{n-2} \alpha_1 K_{n-1} + (-1)^{n-1} K_n \end{aligned}\right\} \quad (6)$$

and considering the limit of this quotient for $n = \infty$ we obtain immediately the result of FREDHOLM.

2. To prove the relation (4), we expand the determinant.

$$\begin{vmatrix} K(xy) & K(xx_1) & \dots & K(xx_n) \\ K(x_1y) & K(x_1x_1) & \dots & K(x_1x_n) \\ \cdot & \cdot & \cdot & \cdot \\ K(x_ny) & K(x_nx_1) & \dots & K(x_nx_n) \end{vmatrix} = K\begin{pmatrix} xx_1 \dots x_n \\ yx_1 \dots x_n \end{pmatrix}$$

according to the elements of the first row, and integrate over the variables $x_1\, x_2 \dots x_n$ between the limits a and b. This gives, as has been remarked already by FREDHOLM

$$I_n = \int_a^b \!..\! \int_a^b K\begin{pmatrix} xx_1 \,..\, x_n \\ yx_1 \,..\, x_n \end{pmatrix} dx_1..dx_n = K(xy) \int_a^b \!..\! \int_a^b K\begin{pmatrix} x_1 \,..\, x_n \\ x_1 \,..\, x_n \end{pmatrix} dx_1..dx_n$$

$$- n \int_a^b K(x\tau_1)d\tau_1 \int_a^b \!..\! \int_a^b K\begin{pmatrix} \tau_1 x_1 \,..\, x_{n-1} \\ yx_1 \,..\, x_{n-1} \end{pmatrix} dx_1..dx_{n-1}\,.$$

By repeating this process we obtain

$$\int_a^b \!..\! \int_a^b K\begin{pmatrix} \tau_1 x_1 \,..\, x_{n-1} \\ yx_1 \,..\, x_{n-1} \end{pmatrix} dx_1..dx_{n-1} = K(\tau_1 y) \int_a^b \!..\! \int_a^b K\begin{pmatrix} x_1 \,..\, x_{n-1} \\ x_1 \,..\, x_{n-1} \end{pmatrix} dx_1..dx_n$$

$$- (n-1) \int_a^b K(\tau_1\tau_2)d\tau_2 \int_a^b \!..\! \int_a^b K\begin{pmatrix} \tau_2 x_1 \,..\, x_{n-2} \\ y\; x_1 \,..\, x_{n-2} \end{pmatrix} dx_1..dx_{n-2}\,.$$

Pursuing in this way, and putting

$$k!\,\alpha_k = \int_a^b \!..\! \int_a^b K\begin{pmatrix} x_1 \,..\, x_k \\ x_1 \,.\, x_k \end{pmatrix} dx_1..dx_k$$

we get, after p operations

$$I_n = n!\,\alpha_n K(xy) - n!\,\alpha_{n-1} K_2(xy) + n!\,\alpha_{n-2} K_3(xy) - .. + (-1)^{p-1} n!\, K_p(xy) +$$

$$+ (-1)^p n(n-1)..(n-p+1) \int_a^b \!..\! \int_a^b K(x\tau_1)K(\tau_1\tau_2)..K(\tau_{p-1}\tau_p)d\tau_1..d\tau_p \times$$

$$\times \int_a^b \!..\! \int_a^b K\begin{pmatrix} \tau_p x_1 \,..\, x_{n-p} \\ y\; x_1 \,..\, x_{n-p} \end{pmatrix} dx_1..dx_{n-p}\,,$$

and, if $p = n - 1$

$$I_n = n!\,[\alpha_n K(xy) - \alpha_{n-1} K_2(xy) + \dots + (-1)^{n-1} \alpha_1 K_n(xy) + (-1)^n K_{n+1}(xy)] \quad (7)$$

from which at once the values B_p may be determined, for

$$B_p = \frac{I_p}{p!} = \frac{1}{p!} \int_a^b \!..\! \int_a^b K\begin{pmatrix} xx_1 \,..\, x_p \\ yx_1 \,..\, x_p \end{pmatrix} dx_1..dx_p\,. \quad (8)$$

Remarking now that

$$K\begin{pmatrix} x x_1 .. x_n \\ y x_1 . x_n \end{pmatrix} = \begin{vmatrix} X_1(x)\ X_2(x)\ ..X_n(x)\ 1 \\ X_1(x_1) X_2(x_1) .. X_n(x_1) 1 \\ . \quad . \quad . \quad . \quad . \quad . \quad . \\ X_1(x_n) X_2(x_n) .. X_n(x_n) 1 \end{vmatrix} \times \begin{vmatrix} Y_1(y)\ Y_2(y)\ ..Y_n(y)\ 0 \\ Y_1(x_1) Y_2(x_1) .. Y_n(x_1) 0 \\ . \quad . \quad . \quad . \quad . \quad . \quad . \\ Y_1(x_n) Y_2(x_n) .. Y_n(x_n) 0 \end{vmatrix}$$

it follows that the first number of (7) is zero. This proves the equation (4) when $p=0$. Writing this result

$$\alpha_n K_1(xs) - \alpha_{n-1} K_2(xs) + ... + (-1)^{n-1} \alpha_1 K_n(xs) + (-1)^n K_{n+1}(xs) = 0,$$

multiplying by $K(sy)\,ds$ and integrating between the limits a and b, we get

$$\alpha_n K_2(xy) - \alpha_{n-1} K_3(xy) + ... + (-1)^{n-1} \alpha_1 K_{n-1}(xy) + (-1)^n K_{n+2}(xy) = 0.$$

Repeating this process it is evident that equation (4) holds for all values of p.

3. If now n is infinite, the equation (5) may be written

$$\Gamma(xy\lambda) = \frac{D(xy\lambda)}{D(\lambda)}$$

where

$$D(xy\lambda) = K(xy) + \sum_1^\infty \frac{(-1)^p \lambda^p}{p!} \int_a^b .. \int_a^b K\begin{pmatrix} x x_1 .. x_p \\ y x_1 .. x_p \end{pmatrix} dx_1 .. dx_p . \quad . \quad (9)$$

and

$$D(\lambda) = 1 + \sum_1^\infty \frac{(-1)^p \lambda^p}{p!} \int_a^b .. \int_a^b K\begin{pmatrix} x_1 .. x_p \\ x_1 .. x_p \end{pmatrix} dx_1 .. dx_p . \quad . \quad . \quad (10)$$

For the proof that the first of these series converges absolutely and uniformly in the square, and that the second converges absolutely for all values of λ we refer to the original memoir of FREDHOLM.

4. The preceding method enables us also to obtain the coefficients of both series in the form which has been discovered by PLEMELJ.

Expanding in the same way as before we have

$$\int_a^b .. \int_a^b K\begin{pmatrix} x_1 x_2 .. x_p \\ x_1 x_2 .. x_p \end{pmatrix} dx_2 .. dx_p = K(x_1 x_1) \int_a^b .. \int_a^b K\begin{pmatrix} x_2 .. x_p \\ x_2 .. x_p \end{pmatrix} dx_2 .. dx_p$$

$$- (p-1) \int_a^b K(x_1 \tau_1) d\tau_1 \int_a^b .. \int_a^b K\begin{pmatrix} \tau_1 x_2 .. x_{p-1} \\ x_1 x_2 .. x_{p-1} \end{pmatrix} dx_2 .. dx_{p-1}$$

$$\int_a^b..\int_a^b K\begin{pmatrix}\tau_1 x_2\,..x_{p-1}\\ x_1\,x_2..x_{p-1}\end{pmatrix}dx_2..dx_{p-1} = K(\tau_1 x_1)\int_a^b..\int_a^b K\begin{pmatrix}x_2...x_{p-1}\\ x_2..x_{p-1}\end{pmatrix}dx_2..dx_{p\;\;1}$$

$$-(p-2)\int_a^b K(\tau_1\tau_2)d\tau_2\int_a^b..\int_a^b K\begin{pmatrix}\tau_2 x_2...x_{p-2}\\ x_1 x_2..x_{p-2}\end{pmatrix}dx_2..dx_{p-2}$$

etc.

Thus, putting

$$\int_a^b K_k(xx)\,dx = a_k$$

and integrating over x_1 between a and b

$$p!\alpha_p = (p-1)!\,a_1\alpha_{p-1} - (p-1)!\,a_2\alpha_{p-2} + (p-1)!\,a_3\alpha_{p-3} - ..$$
$$+ (-1)^p (p-1)!\,a_{p-1}\alpha_1 + (-1)^{p+1}(p-1)!\,a_p\ . \qquad (11)$$

or

$$a_p = a_{p-1}\alpha_1 - a_{p-2}\alpha_2 + a_{p-3}\alpha_3 - ... + (-1)^p a_1\alpha_{p-1} + (-1)^{p+1}p\alpha_p.$$

Hence

$$a_1 = \alpha_1$$
$$a_2 = a_1\alpha_1 - 2\alpha_2$$
$$a_3 = a_2\alpha_1 - a_1\alpha_2 + 3\alpha_3$$
$$. \quad . \quad . \quad . \quad . \quad . \quad .$$
$$a_{p-1} = a_{p-2}\alpha_1 - a_{p-3}\alpha_2 + a_{p-4}\alpha_3 - .. + (-1)^p(p-1)\alpha_{p-1}$$
$$(-1)^p p\alpha_p + a_p = a_{p-1}\alpha_1 - a_{p-2}\alpha_2 + a_{p-3}\alpha_3 - .. + (-1)^p a_1\alpha_{p-1}$$

and eliminating from these $\alpha_1\alpha_2 .. \alpha_{p-1}$

$$p!\,\alpha_p = \begin{vmatrix} a_1 & 1 & 0 & ...\,0 \\ a_2 & a_1 & 2 & ...\,0 \\ a_3 & a_2 & a_1 & ...\,0 \\ . & . & . & . \\ a_{p-1} & a_{p-2} & a_{p-3} & ...\,p-1 \\ a_p & a_{p-1} & a_{p-2} & ...\,a_1 \end{vmatrix} = \begin{vmatrix} a_1 & p-1 & 0 & ...\,0 \\ a_2 & a_1 & p-2 & ...\,0 \\ a_3 & a_2 & a_1 & ...\,0 \\ . & . & . & . \\ a_{p-1} & a_{p-2} & a_{p-3} & ...\,1 \\ a_p & a_{p-1} & a_{p-2} & ...\,a_1 \end{vmatrix}\ . \qquad (12)$$

Eliminating in the same way $\alpha_1\,\alpha_2\,..\,\alpha_p$ from the $p+1$ equations

$$a_1 = \alpha_1$$
$$a_2 = a_1\alpha_1 - 2\alpha_2$$
$$a_3 = a_2\alpha_1 - a_1\alpha_2 + 3\alpha_3$$
$$. \quad . \quad . \quad . \quad . \quad . \quad .$$
$$a_{p-1} = a_{p-2}\alpha_1 - a_{p-3}\alpha_2 + a_{p-4}\alpha_3 - .. + (-1)^p(p-1)\alpha_{p-1}$$
$$a_p = a_{p-1}\alpha_1 - a_{p-2}\alpha_2 + a_{p-3}\,\alpha_3 - .. + (-1)^p a_1\,\alpha_{p-1} + (-1)^{p+1}p\alpha_p$$
$$(-1)^{p-1}B_p + K_{p+1} = K_p\,\alpha_1 - K_{p-1}\alpha_2 + K_{p-2}\alpha_3 - .. + (-1)^p K_2\alpha_{p-1} + (-1)^{p+1}K_1\alpha_p$$

the last being one of the equations (6) we find

$$n\,!\,B_p = \begin{vmatrix} K_1 & p & 0 & \ldots 0 \\ K_2 & a_1 & p-1 & \ldots 0 \\ K_3 & a_2 & a_1 & \ldots 0 \\ K_p & a_{p-1} & a_{p-2} & \ldots 1 \\ K_{p+1} & a_p & a_{p-1} & \ldots a_1 \end{vmatrix} \quad \ldots\ldots \tag{13}$$

The formulae (12) and (13) agree with those of PLEMELJ.

5. If the kernel $K(xy)$ be defined throughout the square so that

$$K(xy) = \frac{I(xy)}{(x-y)^{\alpha}}$$

where $I(xy)$ is finite in the square and $\alpha < \frac{n-1}{n}$, then it may be readily proved that the iterated kernels $K_2\, K_3 \ldots K_{n-1}$ are all infinite for $x = y$, and that the kernels $K_n,\ K_{n+1}, \ldots$ are all finite in the whole square. Likewise all the integrals

$$\int_a^b K_m(xs)\, f(s)\, ds \qquad (m = 1, 2, 3 \ldots \infty)$$

are finite throughout the square.

For this case it is shown by POINCARÉ[1] that FREDHOLM's solution still holds if the determinants

$$K\begin{pmatrix} x_1 & x_2 & \ldots & x_p \\ x_1 & x_2 & \ldots & x_p \end{pmatrix}$$

and

$$K\begin{pmatrix} x & x_1 & \ldots & x_p \\ y & x_1 & \ldots & x_p \end{pmatrix}$$

are modified in the following way.

If by a cycle of k letters $\alpha, \beta, \gamma, \delta \ldots \mu$ is meant the product

$$K(\alpha\beta)\, K(\beta\gamma)\, K(\gamma\delta) \ldots K(\mu\alpha)$$

those products, in expanding the determinants, must be omitted which contain cycles of less than n letters.

Now we wish to show that these modified coefficients may at once be obtained from those of PLEMELJ by substituting therein $a_1 = a_2 = \ldots a_{n-1} = 0$.

For this purpose we note that the equation (4) still holds if K_i be

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[1] Act. Math. Bd. 33.

replaced by a_i as may be seen by putting $y = x$ and integrating between a and b.

Thus

$$a_n a_{p+1} - a_{n-1} a_{p+2} + \dots + (-1)^n a_{p+n+1} = 0 \; (p = 0 \, . \, 1 \, . \, 2 \, . \, .)$$

and this relation proves that $a_1 + a_2 \lambda + a_3 \lambda^2 + \dots$ is a reciprocal series, which may be written

$$a_1 + a_2 \lambda + a_3 \lambda^2 + \dots = \frac{b_0 - b_1 \lambda + b_2 \lambda^2 \dots (-1)^{n-1} b_{n-1} \lambda^{n-1}}{1 - a_1 \lambda + a_2 \lambda^2 - \dots + (-1)^n a_n \lambda^n}$$

where

$$b_p = a_p a_1 - a_{p-1} a_2 + a_{p-2} a_3 - \dots + (-1)^{p-1} a_{p+1} \; (p = 0.1.2..n-1)$$

or, according to (11)

$$b_p = (p+1) \, a_{p+1}.$$

Hence, if n be infinite

$$a_1 + a_2 \lambda + a_3 \lambda^2 + \dots = \frac{a_1 - 2 a_2 \lambda + 3 a_3 \lambda^2 - \dots}{1 - a_1 \lambda + a_2 \lambda^2 - a_3 \lambda^3 - \dots} = - \frac{D'(\lambda)}{D(\lambda)}$$

or

$$D(\lambda) = e^{-a_1 \lambda - \frac{a_2}{2} \lambda^2 - \frac{a_3}{2} \lambda^3 - \dots}$$

Writing this equation

$$D(\lambda) \, e^{a_1 \lambda + \frac{a_2}{2} \lambda^2 + \frac{a_3}{2} \lambda^3 + \dots \frac{a_{n-1}}{n-1} \lambda^{n-1}} = e^{-\frac{a_n}{n} \lambda^n - \frac{a_{n+1}}{n+1} \lambda^{n+1} - \dots} =$$

$$= 1 + (-1)^n \left\{ \Delta_n^0 \frac{\lambda^n}{n!} - \Delta_{n+1}^0 \frac{\lambda^{n+1}}{(n+1)!} + \dots \right\}$$

it is evident that the first member is independent of $a_1 a_2 \dots a_{n-1}$.

If therefore

$$D(\lambda) = 1 - \Delta \lambda + \Delta_2 \frac{\lambda^2}{2!} - \Delta_3 \frac{\lambda^3}{3!} + \dots$$

we have

$$\left(1 - \Delta \lambda + \Delta_2 \frac{\lambda^2}{2!} - \Delta_3 \frac{\lambda^3}{3!} + \dots\right)_{a_1 = a_2 = \dots = a_{n-1} = 0} = 1 + (-1)^n \left\{ \Delta_n^0 \frac{\lambda^n}{n!} - \Delta_{n+1}^0 \frac{\lambda^{n+1}}{(n+1)!} - \dots \right\}$$

or finally

$$\Delta_p^0 = (\Delta_p)_{a_1 = a_2 = \dots = a_{n-1} = 0} \quad \dots \dots \dots \quad (14)$$

and

$$\Delta_1^0 = \Delta_2^0 = \dots = \Delta_{n-1}^0 = 0.$$

In the same way it follows from

$$D(xy\lambda) = D(\lambda) \{ K_1 + \lambda K_2 + \lambda^2 K_3 + \dots \}$$

or

$$D(xy\lambda)\, e^{a_1\lambda + \frac{a_2}{2}\lambda^2 + \frac{a_3}{3}\lambda^3 + \dots + \frac{a_{n-1}}{n-1}\lambda^{n-1}} =$$

$$= e^{-\frac{a_n}{n}\lambda^n - \frac{a_{n+1}}{n+1}\lambda^{n+1} - \dots} \{K_1 + \lambda K_2 + \lambda^2 K_3 \dots\}$$

that the first member of this equation is independent of $a_1 a_2 \dots a_{n-1}$.

Thus assuming

$$D(xy\lambda) = E_0 - E_1\lambda + E_2\frac{\lambda^2}{2!} - E_3\frac{\lambda^3}{3!} + \dots$$

and

$$D(xy\lambda)\, e^{a_1\lambda + \frac{a_2}{2}\lambda^2 + \frac{a_3}{3}\lambda_3 + \dots + \frac{a_{n-1}}{n-1}\lambda^{n-1}} =$$

$$= E_0^0 - E_1^0\lambda + E_2^0\frac{\lambda^2}{2!} - E_3^0\frac{\lambda^3}{3!} + \dots$$

we find

$$\left(E_0 - E_1\lambda + E_2\frac{\lambda^2}{2!} - E_3\frac{\lambda^3}{3!} + \dots\right)_{a_1=a_2=..=a_{n-1}=1} = E_0^0 - E_1^0\frac{\lambda^2}{2!} - E_3^0\frac{\lambda^3}{3!} + \dots$$

that is

$$E_p^0 = (E_p)_{a_1=a_2=..=a_{n-1}=0} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Having thus established the relations (14) and (15) we may conclude that if

$$K(xy) = \frac{I(xy)}{(x-y)^\alpha}\left(\alpha < \frac{n-1}{n}\right)$$

the formulae for $D(xy\lambda)$ and $D(\lambda)$ where the coefficients are written in PLEMELJ's form, still hold if $a_1 = a_2 = \dots = a_{n-1} = 0$.

The same result may at once be deduced from the rule given by POINCARÉ. For if instead of the coefficients of FREDHOLM we take those of PLEMELJ and remark that the k-fold integral of a cycle of k letters always gives

$$\int_a^b \dots \int_a^b K(\alpha\beta)\, K(\beta\gamma) \dots K(\mu\alpha)\, d\alpha \dots d\mu = \int_a^b K_k(\alpha\alpha)\, d\alpha = a_k$$

then it is evident that those terms from PLEMELJ's coefficients must be omitted which contain $a_1\, a_2 \dots a_{n-1}$ or what is equivalent, that in these coefficients must be substituted

$$a_1 = a_2 = \dots = a_{n-1} = 0.$$

Mathematics. — *"The oscillations about a position of equilibrium where a simple linear relation exists between the frequencies of the vibrations".* (Third Part). By H. J. E. Beth. (Communicated by Prof. D. J. Korteweg).

(Communicated in the meeting of December 24, 1910).

§ 1. In my dissertation [1]) were investigated the oscillations about a position of equilibrium of a mechanism with two degrees of freedom where a linear relation exists between the principal frequencies of vibration for which relation the sum of coefficients is $S \leq 4$. In what follows this investigation will be extended to a mechanism with an arbitrary number of degrees of freedom.

In the first place we shall trace the influence of a relation between two of the frequencies of vibration. Then the relations shall be discussed which are possible between 3 or 4 of the frequencies of vibration. Relations of more than 4 of the frequencies of vibration are outside our consideration, as we have always to keep in mind $S \leq 4$.

Relations between two of the frequencies of vibration.

§ 2. We imagine a mechanism with k degrees of freedom. Between the frequencies of vibration n_1 and n_2 of the principal coordinates q_1 and q_2 exists the relation

$$\gamma n_1 = n_2 + \varrho.$$

where $\gamma = 1$, 2 or 3. The remaining $k-2$ principal frequencies of vibration $n_3, n_4, \ldots . n_k$ do not appear in the relation; we suppose moreover that between the k frequencies or between some of them no exact or approximate relation exists except the just mentioned one.

By the *disturbing terms of the first kind* in the equations of movement we shall understand terms which are always disturbing, also when no relation exists. When substituting the expressions for the coordinates by first approximation we find out of such a term a term having the same period and the same phase as the coordinate to which the equation, where the disturbing term appears, relates more in particular. These disturbing terms are of order h^3 or higher.

By *disturbing terms of the second kind* we understand such as owe their disturbing property to the existing relations. When substituting as above we find out of such a term a term corresponding to the coordinate in period but not in phase. These disturbing terms are of order h^{S-1} or higher.

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[1]) Amsterdam, 1910; also These Proceedings, page 618—635 and page 735—750 (1910); Archives Néerlandaises, Séries II, Vol. XV, page 246—283 (1910).

§ 3. $S = 3\,(2n_1 = n_2 + \varrho)$. In general disturbing terms of the second kind of order h^2 appear. So the disturbing terms of the first kind can be left out, because they are at least of order h^3 and because in the equations we use the disturbing terms of the lowest order only. The disturbing terms of order h^2 appear only in the equations for q_1 and q_2, and they contain no other coordinates but q_1 and q_2. On account of this these two equations, in as far as they must be considered to give the first approximation, get the same form as we have formerly found for an arbitrary mechanism with two degrees of freedom only. The coordinates q_1 and q_2 bear themselves as if they were the only coordinates. As in the equations for $q_3, q_4, \ldots\ldots q_k$ no disturbing terms of order h^2 appear, these coordinates bear themselves for first approximation as if no relation existed.

§ 4. $S = 4\,(3n_1 = n_2 + \varrho)$. Both kinds of disturbing terms are at least of order h^3. Disturbing terms of the second kind of order h^3 appear in the equations for q_1 and q_2 only and they contain no other coordinates than q_1 and q_2; so they are the same terms as those which appear in case $S = 4$ for a mechanism with two degrees of freedom as disturbing terms of the second kind.

However it is clear that disturbing terms of the first kind of order h^3 appear in all equations and that they will contain the coordinates $q^3, \ldots\ldots q_k$ as well as q_1 and q_2. We reduce them in the following manner.

In the first equation disturbing terms of the first kind of order h^3 are those with: q_1^3, $q_1^2\ddot{q}_1$, $q_1\dot{q}_1^2$, $q_1 q_2^2$, $q_1 q_3^2 \ldots q_1 q_k^2$, $\ddot{q}_1 q_2^2$, $\ddot{q}_1 q_3^2 \ldots \ddot{q}_1 q_k^2$, $q_1\dot{q}_2^2$, $q_1\dot{q}_3^2 \ldots q_1\dot{q}_k^2$, $q_1 q_2\ddot{q}_2$, $q_1 q_3\ddot{q}_3 \ldots q_1 q_k\ddot{q}_k$.

If we take as solution at first approximation

$$q_r = \frac{\sqrt{\alpha_r}}{n_r}\cos\,(n_r t + 2n_r\beta_r) \quad (r = 1, 2, 3 \ldots k)$$

then in the terms of higher order we may substitute $-n_r^2 q_r$ for $\ddot{q}_r$ and $\alpha_r - n_r^2 q_r^2$ for $\dot{q}_r^2$. We then retain as disturbing terms of the first kind in the first equation only those with

$$\alpha_r q_1,\ q_1^3,\ q_1 q_2^2,\ q_1 q_3^2 \ldots q_1 q_k^2.$$

We then substitute $\dfrac{\alpha_2}{2n_2^2}\,q_1$ etc. for $q_1 q_2^2$.

If we deduce in the same way the disturbing terms of the first kind also in the remaining equations, we shall find that these terms are in the different equations the derivatives resp. according to $q_1, q_2 \ldots q_k$ of

$$\sum_{r=1}^{r=k} A_r q_r^4 + \sum_{r=1}^{r=k} \sum_{s=1}^{s=k} B_{rs} \alpha_r q_s^2,$$

where A_r and B_{rs} represent constants.

So we have shown that there is a function of which the disturbing terms in the equations are the derivatives. If we write it as function of the α's, β's and t and afterwards leave out the terms containing t explicitly, we find:

$$-R = \chi_2 (\alpha_1, \alpha_2, \ldots \alpha_k) + \varrho' h^2 \alpha_2 + m_1 \alpha_1 \sqrt{\alpha_2} \cos 6 n_1 (\beta_1 - \beta_2).$$

Here χ_2 is a homogeneous quadratic function of the α's; the term $\varrho' h^2 \alpha_2$ is inserted in order to take in the wellknown way the residue of relation into account.

The α's and β's must now be determined as functions of t with the aid of the following system of equations:

$$\dot{\alpha}_r = \frac{\partial R}{\partial \beta_r}, \; \dot{\beta}_r = - \frac{\partial R}{\partial \alpha_r}. \; (r = 1, 2, 3, \ldots k).$$

We immediately notice that now also

$$\alpha_1 = - \alpha_2.$$

Hence

$$\alpha_1 + \alpha_2 = \text{constant}.$$

From the absence of $\beta_3, \beta_4 \ldots \beta_k$ in R it is evident that:

$$\dot{\alpha}_3 = \dot{\alpha}_4 = \ldots . = \dot{\alpha}_k = 0.$$

Hence

$$\alpha_3 = \text{constant}, \; \alpha_4 = \text{constant}, \ldots . . \alpha_k = \text{constant}.$$

Here $\dot{\alpha}_1$ and $\dot{\alpha}_2$ have the same form as for the mechanism with two degrees of freedom.

The expressions for $\dot{\beta}_1$ and $\dot{\beta}_2$ contain both, besides the terms which they have for the mechanism with two degrees of freedom, one more linear function of $\alpha_3, \alpha_4, \ldots . \alpha_k$. On account of what was just found these functions can be reduced to constants of order h^2. Let $m_1 h^2$ be this constant term in the second member of the equation for $\dot{\beta}_1$, $m_2 h^2$ the term in the second member of the equation for $\dot{\beta}_2$. This is then the influence of these terms that the frequency of vibration n_1 must be increased by $m_1 h^2$ and the residue of relation by $6 n_1 (m_2 - m_1) h^2$.

Then $\alpha_1, \alpha_2, \beta_1$ and β_2 are determined out of the same equations as in the case of the mechanism with two degrees of freedom. The coordinates of q_1 and q_2 behave here too as if they were the only ones. The influence of the k—2 remaining degrees of freedom consists in a modification of n_1 and n_2, which modification is of order h^2 and dependent on the amplitudes of the remaining k—2 vibrations.

Then $\dot{\beta}_3, \dot{\beta}_4, \ldots\ldots \beta_4$ are, as the form of R tells us, linear functions of $\alpha_1, \alpha_2 \ldots\ldots \alpha_k$. As $\alpha_3, \alpha_4 \ldots\ldots \alpha_k$ are constant and as α_2 can be expressed in α_1 we can write $\dot{\beta}_3, \dot{\beta}_4, \ldots\ldots \dot{\beta}_k$ as linear functions of α_1. So the coordinates $q_3, q_4 \ldots\ldots q_k$ feel the influence of the relation, however only in the phase, not in the amplitude. As α_1 (just as α_2, β_1, and β_2) was determined before already as function of t, we can also determine $\beta_3, \beta_4, \ldots\ldots \beta_k$. So the problem has been reduced to quadratures.

§ 5. $S = 2\,(n_1 = n_2 + \varrho)$. All disturbing terms which we have to regard are again of order h^3. For this case the peculiarity appears that all disturbing terms of the second kind must be regarded at the same time as disturbing of the first kind. So a term $q_1 q_2{}^2$ in the first equation gives as disturbing terms a term with $\cos\,(nt + 2n_1\beta_2)$ and one with $\cos\,(nt + 4n_1\beta_2 - 2n_1\beta_1)$.

Just as was done above for the case $S = 4$ we can prove easily also for this case that, apart from a modification of their frequency of vibration, the coordinates q_1 and q_2 behave as if we had to do with a mechanism with two degrees of freedom, whilst the remaining coordinates feel the influence of relation in their phase, but not in their amplitude.

RELATION BETWEEN THREE OF THE FREQUENCIES OF VIBRATION FOR WHICH $S = 3$.

§ 6. The only relation which for $S = 3$ remains to be discussed runs:

$$n_1 + n_2 - n_3 = \varrho.$$

Just as was done in § 3 for the case of a relation between two of the frequencies of vibration for which $S = 3$ we can also show here, that at first approximation only the coordinates q_1, q_2, and q_3 feel the influence of the relation and that q_1, q_2, and q_3 behave as if they were the only coordinates. So we can restrict ourselves to a mechanism with but three degrees of freedom; q_1, q_2, and q_3 are the principal coordinates.

As in the equations of motion terms of order h^2 appear already among the disturbing terms we need not take into account any terms of a higher order than h^3 in the expressions for the kinetic energy and the potential function. Hence

$$T = \tfrac{1}{2} \sum_{r=1}^{r=3} \dot{q}_r{}^2 + \tfrac{1}{2} \sum_{r=1}^{r=3} \sum_{s=1}^{s=3} (P_{rr}\dot{q}_r{}^2 + 2\,P_{rs}\dot{q}_r\,\dot{q}_s),$$

$$U = \tfrac{1}{2} \sum_{r=1}^{r=3} n_r^2 q_r^2 + H_3 (q_1, q_2, q_3),$$

where H_3 represents a homogeneous function of order three, and

$$P_{rs} = a_{rs} q_1 + b_{rs} q_2 + c_{rs} q_3.$$

The equation of LAGRANGE for the coordinate q_1 runs:

$$\ddot{q}_1 + n_1^2 q_1 = -\sum_{r=1}^{r=3} P_{1r} \ddot{q}_r - \sum_{r=1}^{r=3} (b_{1r} \dot{q}_2 + c_{1r} \dot{q}_3) \dot{q}_r + \tfrac{1}{2} \sum_{r=1}^{r=3} a_{rr} \dot{q}_r^2 + a_{23} \dot{q}_2 \dot{q}_3 - \frac{\partial H_3}{\partial q_1}.$$

When in the terms of the second member $\ddot{q}_r$ is replaced by $-n_r^2 q_r$, then in the case of the supposed relation we have to regard as disturbing in this equation the terms with $\dot{q}_2 \dot{q}_3$ and those with $q_2 q_3$. Omitting all the remaining terms of a higher order the equation becomes:

$$\ddot{q}_1 + n_1^2 q_1 = (c_{12} n_2^2 + b_{13} n_3^2 - p) q_2 q_3 - (-a_{23} + b_{13} + c_{12}) \dot{q}_2 \dot{q}_3.$$

(p being the coefficient of the term $q_1 q_2 q_3$ in H_3).

We may now replace $q_2 q_3$ by $n_2 n_3 q_2 q_3$, because these two products furnish the same disturbing term when we substitute for q_2 and q_3 the expressions to be taken at first approximation. We then find:

$$\ddot{q}_1 + n_1^2 q_1 = \{a_{23} n_2 n_3 + b_{13} n_3 (n_3 - n_2) + c_{12} n_2 (n_2 - n_3) - p\} q_2 q_3.$$

Putting in the second member $n_1 + n_2 - n_3 = 0$ we finally find:

$$\ddot{q}_1 + n_1^2 q_1 = (a_{23} n_2 n_3 + b_{13} n_1 n_3 - c_{12} n_1 n_2 - p) q_2 q_3.$$

In this way we can also simplify the two other equations; we must then bear in mind that in the second equation $\dot{q}_1 \dot{q}_3$ must be replaced by $n_1 n_3 q_1 q_3$, in the third equation however $q_1 q_2$ by $-n_1 n_2 q_1 q_2$.

The result is that the equations of motion are to be written as follows:

$$\ddot{q}_r + n_r^2 q_r - \frac{\partial R}{\partial q_r} = 0 \qquad (r = 1, 2, 3). \quad . \quad . \quad . \quad . \quad (1)$$

where

$$-R = \{p - (a_{23} n_2 n_3 + b_{13} n_1 n_3 - c_{12} n_1 n_2)\} q_1 q_2 q_3.$$

If, however, we take as abridged 3rd equation

$$\ddot{q}_3 + (n_1 + n_2)^2 q_3 = 0,$$

then we find:

$$-R = \{p - (a_{23} n_2 n_3 + b_{13} n_1 n_3 - c_{12} n_1 n_2)\} q_1 q_2 q_3 -$$
$$- \varrho (n_1 + n_2) q_3^2 = p' q_1 q_2 q_3 - \varrho (n_1 + n_2) q_3^2$$

Pure relation $n_1 + n_2 - n_3 = 0$.

§ 7. As first approximation of system (1) we take:

$$q_1 = \frac{\sqrt{\alpha_1}}{n_1} \cos (n_1 t + 2 n_1 \beta_1),$$

$$q_2 = \frac{\sqrt{\alpha_2}}{n_2} \cos (n_2 t + 2 n_2 \beta_2),$$

$$q_3 = \frac{\sqrt{\alpha_3}}{n_1 + n_2} \cos \{(n_1 + n_2) t + 2 (n_1 + n_2) \beta_3\}.$$

The α's must necessarily be positive quantities and in general do not become zero during the motion. We now write $-R = p' q_1 q_2 q_3$ as a function of the α's, β's, and t, and we then omit the terms, containing t explicitly. Then we find:

$$-R = p'' \sqrt{\alpha_1 \alpha_2 \alpha_3} \cos \varphi,$$

where

$$p'' = \frac{p'}{4 n_1 n_2 (n_1 + n_2)},$$

$$\varphi = 2 \{n_1 \beta_1 + n_2 \beta_2 - (n_1 + n_2) \beta_3\}.$$

The system of equations, determining the variability of the α's and β's, runs:

$$\left.\begin{aligned}
\dot{\alpha}_1 &= 2 n_1 p'' \sqrt{\alpha_1 \alpha_2 \alpha_3} \sin \varphi, & \dot{\beta}_1 &= \frac{p''}{2} \frac{\sqrt{\alpha_1 \alpha_2 \alpha_3}}{\alpha_1} \cos \varphi, \\
\dot{\alpha}_2 &= 2 n_2 p'' \sqrt{\alpha_1 \alpha_2 \alpha_3} \sin \varphi, & \dot{\beta}_2 &= \frac{p''}{2} \frac{\sqrt{\alpha_1 \alpha_2 \alpha_3}}{\alpha_2} \cos \varphi, \\
\dot{\alpha}_3 &= -2 (n_1 + n_2) p'' \sqrt{\alpha_1 \alpha_2 \alpha_3} \sin \varphi, & \dot{\beta}_3 &= \frac{p''}{2} \frac{\sqrt{\alpha_1 \alpha_2 \alpha_3}}{\alpha_3} \cos \varphi,
\end{aligned}\right\} \quad . \; . \; . \quad (2)$$

An integral of this system is:

$$\sqrt{\alpha_1 \alpha_2 \alpha_3} \cos \varphi = \mathit{constant} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

Furthermore we notice that:

$$\frac{\dot{\alpha}_1}{n_1} = \frac{\dot{\alpha}_2}{n_2} = - \frac{\dot{\alpha}_3}{n_1 + n_2}.$$

$$\dot{\alpha}_1 + \dot{\alpha}_2 + \dot{\alpha}_3 = 0.$$

Therefore:

$$\frac{\alpha_1}{n_1} - \frac{\alpha_2}{n_2} = C_2 h^2, \quad \frac{\alpha_1}{n_1} + \frac{\alpha_3}{n_1 + n_2} = C_3 h^2, \quad \frac{\alpha_2}{n_2} + \frac{\alpha_3}{n_1 + n_2} = (C_3 - C_2) h^2 \quad (4)$$

$$\alpha_1 + \alpha_2 + \alpha_3 = \mathit{constant}. \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

Here C_2 and C_3 are constants; C_3 is positive and $C_3 > C_2$. We suppose C_2 to be positive too, which does not imply a restriction; for if C_3 were negative, we should have but to exchange the coordinates q_1 and q_2.

If we put

$$\frac{\alpha_1}{n_1} = \xi h^2,$$

then

$$\frac{\alpha_2}{n_2} = (\xi - C_2)h^2, \qquad \frac{\alpha_3}{n_1 + n_2} = (C_3 - \xi)h^2.$$

This gives to (3) the form:

$$\sqrt{\xi(\xi - C_2)(C_3 - \xi)}\, \cos\varphi = k, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where k represents a constant.

The first equation of (2) becomes by introduction of ζ:

$$\dot{\xi} = 2p'' \sqrt{n_1 n_2 (n_1 + n_2)}\, h \sqrt{\xi(\xi - C_2)(C_3 - \zeta)}\, \sin\varphi \quad . \quad . \quad (7)$$

Elimination of φ between (6) and (7) furnishes

$$\frac{d\xi}{\pm\sqrt{\xi(\xi - C_2)(C_3 - \xi) - k^2}} = 2p'' \sqrt{n_1 n_2 (n_1 + n_2)}\, h dt.$$

On account of this ζ can be determined as function of t, which makes α_1, α_2, and α_3 to be known; then φ can be found out of (3); finally β_1, β_2, and β_3 out of (2).

§. Let us suppose relation (6):

$$\sqrt{\xi(\xi - C_2)(C_3 - \xi)}\, \cos\varphi = k$$

to represent a curve on polar coordinates; we take ξ as radius vector, φ as polar angle.

As α_1, α_2, and α_3 are positive, ξ, $\xi - C_2$ and $C_3 - \xi$ are positive, ξ remains between C_2 and C_3. So we have to regard only curves situated between the circles $\xi = C_2$ and $\xi = C_3$.

The curves remain on the right or on the left of O according to k being positive or negative. In fig. 1 the curves have been drawn for definite values of C_2 and C_3, for some values of k.

The distances of the points of intersection of a curve with the axis of the angles is found as the positive roots of the equation:

$$\xi(\xi - C_2)(C_3 - \xi) - k^2 = 0.$$

For a given value of C_2 and C_3 there is a maximal value of k^2, for which this equation has two equal roots and below which it has 3 real ones. For this value the curve has contracted to an isolated point. This concerns a special case of motion.

Another special case we have for $k^2 = 0$. Degeneration takes place to the point $\xi = 0$, the circles $\xi = C_2$ and $\xi = C_3$, and the right line $\cos\varphi = 0$.

Further more there are special cases for special values of C_2 and

C_3. If $C_2 = C_3$, then of necessity $k = 0$; so this belongs to the second special case. If $C_2 = 0$, then by putting $\zeta = C_3\zeta'$ the relation (6) passes into the one which we had with the mechanism with two degrees of freedom, for which $n_2 = n_1$.

The special cases will be discussed in § 14.

§ 9. *Osculating curves.* In order to illustrate the motion of the mechanism somewhat better, we use an image point.

To this end we choose the point whose rectangular coordinates x, y, and z are at an arbitrary moment equal to the values of the principal coordinates q_1, q_2, and q_3 at that moment. The motion of this point is then given by

$$x = \frac{\sqrt{a_1}}{n_1} \cos(n_1 t + 2n_1\beta_1),$$

$$y = \frac{\sqrt{a_2}}{n_2} \cos(n_2 t + 2n_2\beta_2),$$

$$z = \frac{\sqrt{a_3}}{n_1 + n_2} \cos\{(n_1+n_2)\,t + 2\,(n_1+n_2)\,\beta_3\}.$$

By eliminating t between these equations two by two and by ascribing to the a's and β's, the values at a definite moment, we find the projections of the osculating curves on the planes of coordinates.

These projections are LISSAJOUS curves; the osculating curves themselves we can call LISSAJOUS twisted curves.

§ 10. Such a twisted curve remains enclosed inside a rectangular parallelopiped bounded by the planes:

$$x = \pm\frac{\sqrt{a_1}}{n_1}\,,\; y = \pm\frac{\sqrt{a_2}}{n_2}\,,\; z = \pm\frac{\sqrt{a_3}}{n_1 + n_2}\,.$$

In consequence of the variability of the a's this enclosed parallelopiped varies continually. The vertices move along a twisted curve, which according to (3) projects itself on the XY-plane as a hyperbola, on the XZ and on the YZ-plane as an ellipse. Out of (5) follows that this curve is situated on an ellipsoid, whose axes lying on the axes of coordinates are in the ratio:

$$\frac{1}{n_1} : \frac{1}{n_2} : \frac{1}{n_1 + n_2}\,.$$

As the a's change periodically between definite limits, the vertices will move to and fro along the above mentioned twisted curve between two extreme positions. (fig. 2).

§ 11. Besides on the α's the form of an osculating curve depends moreover on the β's. However for an osculating curve described in a definite parallelopiped it depends not on 3, but only on 2 quantities, as is evident when we change the origin of time. We can get:

$$x = \frac{\sqrt{\alpha_1}}{n_1} \cos \{n_1 t + 2(n_1\beta_1 - n_1\beta_3)\},$$

$$y = \frac{\sqrt{\alpha_2}}{n_2} \cos \{n_2 t + 2(n_2\beta_2 - n_2\beta_3)\},$$

$$z = \frac{\sqrt{\alpha_3}}{n_1+n_2} \cos (n_1+n_2)\, t.$$

The form of the osculating curve evidently depends on the quantities $\beta_1 - \beta_3$ and $\beta_2 - \beta_3$. So if we put:

$$\frac{\sqrt{\alpha_1}}{n_1} = A\,,\quad \frac{\sqrt{\alpha_2}}{n_2} = B\,,\quad \frac{\sqrt{\alpha_3}}{n_1+n_2} = C,\ 2(n_1\beta_1 - n_1\beta_3) = a,\ 2(n_2\beta_2 - n_2\beta_3) = b,$$

then we find

$$\left.\begin{aligned} x &= A \cos (n_1 t + a), \\ y &= B \cos (n_2 t + b), \\ z &= C \cos (n_1 + n_2)\, t. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

It is evident out of (7) that in the extreme parallelopipeds curves are described for which $\sin \varphi = 0$. So for these curves

$$2(n_1\beta_1 + n_2\beta_2 - n_1\beta_3 - n_2\beta_3) = l\pi.$$

where l is an integer,

$$a + b = l\pi$$
$$b = l\pi - a.$$

So the curves described in the extreme parallelopipeds are given by:

$$\left.\begin{aligned} x &= A \cos (n_1 t + a), \\ y &= B \cos (n_2 t - a + l\pi), \\ z &= C \cos (n_1 + n_2)\, t. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

§ 12. The literature concerning the LISSAJOUS twisted curves seems to restrict itself to a paper of A. RIGHI (Il Nuovo Cimento, vol IX and X, 1873). RIGHI discusses only the case that the periods of the three mutually perpendicular vibrations have a common measure and he investigates which properties of symmetry these curves can have.

Let us put in (8) $t = +\tau$ and $t = -\tau$ and let us call the values of x, y, and z belonging to these values of t, respect. x_1, y_1, z_1 and x_2, y_2, z_2, then we find

$$\tfrac{1}{2}(x_1 + x_2) = A \cos a \cos n_1\tau \ , \ \tfrac{1}{2}(y_1 + y_2) = B \cos b \cos n_2\tau \ , \ z_1 = z_2 .$$

The curve represented by (8) has therefore with respect to directions of chords parallel to the XY-plane as diameter a curve represented by the equations:

$$\left.\begin{aligned} x_3 &= A' \cos n_1 t, \\ y_3 &= B' \cos n_2 t, \\ z_3 &= C \cos (n_1 + n_2)\, t \end{aligned}\right\} \quad . \ . \ . \ . \ . \ . \quad (10)$$

where

$$A' = A \cos a \ , \ B' = B \cos b .$$

To investigate the curves represented by (8) we can start from the simple curves represented by (10). In fig. 3 such a curve is given perspectively, in fig. 4 (continuous lines) by projections for the case that n_1 and n_2 are commensurable and that we have $n_1 = 2n_2$; the twisted curve begins and ends in two vertices of the circumscribed parallelopiped and is described backwards and forwards.

When a curve (10) is constructed we must bear in mind that

$$x = x_3 - \delta_1 \sin n_1 t \ , \ y = y_3 - \delta_2 \sin n_2 t \ , \ z = z_3 ,$$

where

$$\delta_1 = A \sin a \ , \ \delta_2 = B \sin b$$

So we can think the curve (8) as described by a point moving along the curve (10) and vibrating at the same time according to the X- and Y-direction.

From this we can see how the osculating curve changes for increasing values of a and b, and we can make out when it shows double points. In fig. 4 the projections are represented (dotted lines) of an osculating curve for $n_1 = 2n_2$ and small values of a and b.

§ 13. For the curves represented by (9) exists a simple method to construct the ZX- and ZY-projections, when the XY-projection is given. We can imagine l as even; the curves for odd values of l are the mirror image of the curves for even values of l with respect to the XZ-plane. The XY-projection is an entirely arbitrary LISSAJOUS curve; for $t = 0$ the projection of the point is on a diagonal of the circumscribed rectangle.

Now however follows out of (9)

$$\cos^{-1}\frac{z}{C} = \cos^{-1}\frac{x}{A} + \cos^{-1}\frac{y}{B} .$$

In fig. 5 is given how for every point on the XY-projection z is to be constructed. It is easy to show, that the points of intersection of (9) with the XY-plane lie on the ellipse:

$$\frac{x^2}{A^2} \quad \frac{y^2}{B^2} = 1.$$

The points where the curve touches the planes $z = \pm C$ are projected in the right lines

$$\frac{x}{A} = \pm \frac{y}{B}.$$

§ 14. *Special cases.* At the conclusion of § 8 the special cases were named which may appear. They are:

A. *For given values of C_2 and C_3 we find $k = 0$.* The relation

$$\sqrt{\alpha_1 \alpha_2 \alpha_3} \cos \varphi = 0$$

allows of various possibilities.

1. One of the α's is continually zero. Not one of these forms of motion, however, proves to be possible on substitution into (1).

2. $\cos \varphi = 0$; φ is continually $\frac{\pi}{2}$ or $\frac{3\pi}{2}$. The form of motion changes periodically between those for which $\zeta = C_2$ $(\alpha_2 = 0)$ and those for which $\zeta = C_3$ $(\alpha_3 = 0)$.

B. *For given C_2 and C_3 we find k^2 maximum.* Here ζ is constant, so the α's are also constant: the circumscribed parallelopiped does not change. The β's increase uniformly with the time; the osculating curve changes its form; $\sin \varphi = 0$ remains however. The osculating curve is thus represented by (9); α increases uniformly with the time.

C. *C_2 is equal to zero.* Then $\frac{\alpha_1}{n_1} = \frac{\alpha_2}{n_2}$. The movement of the vertices of the circumscribed parallelopiped takes place along a plane curve; the plane passes through the Z-axis. When $C_2 = 0$ and at the same time $k = 0$, then the form of the movement approaches asymptotically the Z vibration.

D. $C_2 = C_3$. An X-vibration continually takes place.

Approximated relation $n_1 + n_2 - n_3 = \varrho$.

§ 15. We must imagine ϱ to be of order h. Now

$$- R = p' q_1 q_2 q_3 - (n_1 + n_2) \varrho q_3^2.$$

As first approximation we take for q_1, q_2, and q_3 the same expressions as in the case of the pure relation. We find for R as function of the α's and β's

$$- R = p' \sqrt{\alpha_1 \alpha_2 \alpha_3} \cos \varphi - \frac{\varrho}{2(n_1 + n_2)} \alpha_3.$$

We can again write down the system of equations which indicates the variability of the α's and β's. This system has again as integrals:

$$\frac{\alpha_1}{n_1} - \frac{\alpha_2}{n_2} = constant, \quad \frac{\alpha_1}{n_1} + \frac{\alpha_3}{n_1 + n_2} = constant, \quad \frac{\alpha_2}{n_2} + \frac{\alpha_3}{n_1 + n_2} = constant\,,$$

$$\alpha_1 + \alpha_2 + \alpha_3 = constant.$$

Let us again put

$$\frac{\alpha_1}{n_1} = \zeta h^2, \quad \frac{\alpha_2}{n_2} = (\zeta - C_2)\,h^2, \quad \frac{\alpha_3}{n_1 + n_2} = (C_3 - \zeta)\,h^2,$$

then the integral $R = constant$ takes the form:

$$\sqrt{\zeta(\zeta - C_2)(C_3 - \zeta)}\cos\varphi = \varrho'\,(k - \zeta),$$

where k represents a constant and

$$\varrho' = \frac{\varrho}{2p''\sqrt{n_1 n_2 (n_1 + n_2) h}}.$$

We now see easily in what way the coordinates are to be found as functions of time.

§ 16. A survey of the general and special cases which can appear, as well as an insight into the manner in which the transition takes place on one hand to the case of the pure relation, on the other hand to the general case, where no relation exists, is to be obtained by representing the relation between ζ and φ on polar coordinates, ζ being the radius vector, φ the polar angle. In

$$\sqrt{\zeta(\zeta - C_2)(C_3 - \zeta)}\cos\varphi = \varrho'\,(k - \zeta)$$

we may represent ϱ' as positive; for the curves for negative values of ϱ' are the mirror images with respect to the right line $\varphi = \frac{\pi}{2}$ of the curves for positive values of ϱ'.

We give to C_2 and C_3 constant values and we find for a certain value of ϱ' the forms of the curves satisfying the different possible values of k. We then see how this system of curves varies when ϱ' passes through all values from very little to very large.

For every value of ϱ three cases can be distinguished:

1. $k > C_3$. As ζ remains smaller than C_3, the second member, so also $\cos\varphi$, remains positive. Curves on the right of O.

2. $k < C_2$. As ζ remains larger than C_2, the second member, so also $\cos\varphi$, remains negative. Curves on the left of O.

3. $C_2 < k < C_3$. The second member, therefore also $\cos\varphi$, becomes zero for $\zeta = k$. Curves which surround O.

The curves represented by the above relation lie therefore either entirely on one side of O, or they surround O.

The domains of the plane occupied by these different kinds of curves are bounded by the curves which correspond to $k = C_2$ and $k = C_3$.

For these values of k a degeneration takes place.

For $k = C_2$ in:

$$\zeta = C_2 \text{ and } \sqrt{\zeta (C_3 - \zeta)}\, cos\, \varphi = - \varrho' \sqrt{\zeta - C_2}.$$

The latter curve lies on the left of O, it begins and ends in the points: $\zeta = C_2$, $\varphi = \pm \frac{\pi}{2}$.

For $k = C_3$ in:

$$\zeta = C_3 \text{ and } \sqrt{\zeta (\zeta - C_2)}\, cos\, \varphi = \varrho' \sqrt{C_3 - \zeta}.$$

The latter curve lies on the right of O; it commences and ends on the points: $\zeta = C_3$, $\varphi = \pm \frac{\pi}{2}$.

To investigate how the system of curves varies when ϱ' is changed, it is sufficient to investigate the variation of the degenerated curves. The result is, that the domain of the curves surrounding O is very small for small values of ϱ' and it extends according as ϱ' increases, so that those curves are most important for great values of ϱ'.

So we have for small values of ϱ' by preference the case, that φ moves to and fro between two extreme opposite values, for great values of ϱ' by preference the case that assumes all values.

Furthermore we notice that according as ϱ' increases the curves surrounding O as centre, i. o. w. ξ and on account of this the a's vary but little. We thus approach the general case where ϱ' has become so great, that we can no longer speak of a relation.

Here too we get for each value of ϱ' for the maximal and minimal value of k an isolated point on the axis of the angles.

Fig. 6 gives some curves for a rather small value of ϱ', fig. 7 for a rather great value of ϱ'; the —·— lines indicate the degenerated curves.

RELATIONS BETWEEN 3 OF THE FREQUENCIES OF VIBRATION FOR WHICH $S = 4$.

§ 17. Two of these relations have to be discussed, namely:

$$(A) \qquad n_1 + 2n_2 - n_3 = \varrho,$$

$$(B) \quad - n_1 + 2n_2 - n_3 = \varrho.$$

We commence with the determination of the disturbing terms of the second kind in the equations of motion. These contain no other coordinates than q_1, q_2, and q_3, and they appear only in the equations of motion which refer more in particular to these coordinates. So it is clear that to determine the disturbing terms of the second kind we can restrict ourselves to a mechanism with three degrees of freedom.

In the equations there are no disturbing terms among the terms of order h^2; terms of a higher order than h^3 are not inserted. Hence we can write the potential function and the kinetic energy as follows:

$$U = \tfrac{1}{2} \sum_{r=1}^{r=3} n_r^2 q_r^2 + H_4 (q_1, q_2, q_3),$$

$$T = \tfrac{1}{2} \sum_{r=1}^{r=3} \dot{q}_r^2 + \tfrac{1}{2} \sum_{r,s=1}^{r,s=3} (P_{rr} \dot{q}_r^2 + 2 P_{rs} \dot{q}_r \dot{q}_s),$$

where H_4 represents a homogeneous function of degree 4, and

$$P_{rs} = \tfrac{1}{2} a_{rs} q_1^2 + \tfrac{1}{2} b_{rs} q_2^2 + \tfrac{1}{2} c_{rs} q_3^2 + e_{rs} q_1 q_2 + f_{rs} q_1 q_3 + h_{rs} q_2 q_3 .$$

If e.g. we write the equation of motion for q_1, then for the relations (A) and (B) the following terms

$$q_2^2 q_3 , \; q_2 \ddot{q}_2 q_3 , \; q_2^2 \ddot{q}_3 , \; \dot{q}_2^2 q_3 \text{ and } q_2 \dot{q}_2 q_3 ,$$

are to be regarded as disturbing.

Let us replace in these terms $\ddot{q}_2$ by $- n_3^2 q_2$, $\ddot{q}_3$ by $- n_2^2 q_3$, $\dot{q}_1^2$ by $- n_2 q_2^2$, and $\dot{q}_2 \dot{q}_3$ by $n_2 n_3 q_2 q_3$.

Let us omit all non-disturbing terms of order h^3 and let us make use in the disturbing terms of the relation $n_1 \pm 2n_2 \mp n_3 = 0$ (which is permissible, as ϱ is of order h^2); we then find that the first equation can be written as follows:

$$\ddot{q}_1 + n_1^2 q_1 = (\mp n_1 n_2 h_{12} \pm \tfrac{1}{2} n_1 n_3 b_{13} - \tfrac{1}{2} n_2^2 f_{22} - n_2 n_3 e_{23} - p) q_2^2 q_3 +$$

disturbing terms of the first kind (p being the coefficient of a term $q_1 q_2^2 q_3$ in U).

Of the $\mp$ and $\pm$ signs the top one must be taken in the case of the relation (A), the bottom one in the case of the relation (B).

When determining the disturbing terms of the second kind in the equations q_2 and q_3, and when reducing these terms according to the method given just now, we find as result that the disturbing terms are the derivatives of one and the same function, namely of

$$p' q_1 q_2^2 q_3 ,$$

where

$$p' = p \pm n_1 n_2 h_{12} \mp n_1 n_3 b_{13} + \tfrac{1}{2} n_2^2 f_{22} - n_2 n_3 e_{23} .$$

This part of the function of disturbance can be again expressed in the same manner in the α's and the β's.

As disturbing terms of the first kind we have but to take the terms, which we have determined in § 4. For those terms are independent of the relation.

So we find that the disturbing function expressed in the α's and the β's takes the following form:

$$-R = \chi_2 (\alpha_1, \alpha_2, \ldots \alpha_k) + \varrho' h^2 \alpha_3 + m_1 \alpha_2 \sqrt{\alpha_1 \alpha_3} \cos \varphi,$$

where again χ_2 represents a homogeneous, quadratic function of the α's.

The second term is inserted because we take as first approximation:

$$q_1 = \frac{\sqrt{\alpha_1}}{n_1} \cos (n_1 t + 2n_1 \beta_1),$$

$$q_2 = \frac{\sqrt{\alpha_2}}{n_2} \cos (n_2 t + 2n_2 \beta_2),$$

$$q_3 = \frac{\sqrt{\alpha_3}}{2n_2 \pm n_1} \cos \{(2n_2 \pm n_1) t + 2 (2n_2 \pm n_1) \beta_3\}; \text{ etc.}$$

Furthermore we find

$$\varphi = \pm 2n_1 \beta_1 + 4n_2 \beta_2 - 2(2n_2 \pm n_1) \beta_3 = \pm 2n_1 (\beta_1 - \beta_3) + 4n_2 (\beta_2 - \beta_3).$$

§ 18. We can again suppose the differential equations written down, determining the variability of the α's and β's. We then immediately find:

$$\alpha_4 = constant, \quad \alpha_5 = constant, \ldots \ldots \ldots \alpha_k = constant.$$

However, $\beta_4, \beta_5 \ldots \beta_k$ are variable. The coordinates $q_4, q_5 \ldots q_k$ experience the influence of the relation in their phase, but not in their amplitude.

Let us regard in particular the equations for $\dot{\alpha}_1$, $\dot{\alpha}_2$ and $\dot{\alpha}_3$:

$$\dot{\alpha}_1 = \pm 2 m_1 n_1 \alpha_2 \sqrt{\alpha_1 \alpha_3} \sin \varphi,$$

$$\dot{\alpha}_2 = + 4 m_1 n_2 \alpha_2 \sqrt{\alpha_1 \alpha_3} \sin \varphi,$$

$$\dot{\alpha}_3 = - 2(2n_2 \pm n_1) m_1 \alpha_2 \sqrt{\alpha_1 \alpha_3} \sin \varphi.$$

We deduce from this:

$$\mp \frac{\dot{\alpha}_1}{n_1} = - \frac{\dot{\alpha}_2}{2n_2} = \frac{\dot{\alpha}_3}{2n_2 \pm n_1},$$

$$\dot{\alpha}_1 + \dot{\alpha}_2 + \dot{\alpha}_3 = 0.$$

§ 19. *Case A.*

$$\frac{\alpha_1}{n_1} - \frac{\alpha_2}{2n_2} = (C_1 - C_2) h^2, \quad \frac{\alpha_2}{2n_2} + \frac{\alpha_3}{2n_2 + n_1} = C_2 h^2, \quad \frac{\alpha_1}{n_1} + \frac{\alpha_3}{2n_2 + n_1} = C_1 h^2,$$

where C_1 and C_2 are positive constants.

If we put

$$\alpha_3 = (2n_2 + n_1) h^2 \xi,$$

we then find

$$a_1 = n_1 (C_1 - \xi) h^2, \quad a_2 = 2n_2 (C_2 - \xi) h^2.$$

The integral $R =$ constant then takes the form:

$$(C_2 - \xi) \sqrt{\xi (C_1 - \xi)} \cos \varphi = p \xi^2 + q \xi + r.$$

Case B.

$$\frac{a_1}{n_1} + \frac{a_2}{2n_2} = C_1 h^2, \quad \frac{a_2}{2n_2} + \frac{a_3}{2n_2 - n_1} = C_3 h^2, \quad \frac{a_3}{2n_2 - n_1} - \frac{a_1}{n_1} = (C_3 - C_1) h^2.$$

where C_1 and C_3 are positive constants.

If we put

$$a_2 = 2n_2 h^2 \xi.$$

then we find

$$a_1 = n_1 (C_1 - \xi) h^2 \ , \ a_3 = (2n_2 - n_1)(C_3 - \xi) h^2.$$

The integral $R =$ constant gets the form:

$$\xi \sqrt{(C_1 - \xi)(C_3 - \xi)} \cos \varphi = p \xi^2 - q \xi + r.$$

§ 20. In case A we find that ξ lies continually between 0 and C_1 or between 0 and C_2 according as C_1 or C_2 is the smaller. In Case B we find that ξ lies continually between 0 and C_1 or between 0 and C_3 according as C_1 or C_3 is the smaller.

When again we represent the relations between ξ and φ as polar coordinates, we find curves of quite the same kind as in the case of a mechanism with two degrees of freedom for which $n_2 = 3n_1$.

So there are curves which do not enclose O and which therefore relate to forms of motion, where φ runs to and fro between two limits; and curves which do enclose O and which therefore relate to forms of motion, where φ takes all values. The transition is formed by a curve, having a double point on the axis of the angles; this points to a particular case, where the form of motion tends asymptotically to a movement where $\sin \varphi = 0$ and ξ is constant. To another special case the isolated point refers situated on the axis of the angles: it points to a form of motion, where $\sin \varphi = 0$ and where ξ is constant.

§ 21. *Osculating curves.* The osculating curves of the image point are again LISSAJOUS twisted curves. The vertices of the circumscribed parallelopiped move along a twisted curve lying on an ellipsoid, whose axes lying along the coordinate axes have lengths proportional to $\frac{1}{n_1} : \frac{1}{n_2} : \frac{1}{2n_2 \pm n_1}$; the twisted curve projects itself in case A on the XY-plane as a hyperbola, on the YZ- and the ZY-plane as an ellipse, in case B on the XZ-plane as a hyperbola on the XY- and the YZ-plane as an ellipse.

The osculating curve described in a definite parallelopiped can be given in the equations

$$x = A \cos (n_1 t + a) ,$$
$$y = B \cos (n_2 t + b) ,$$
$$z = C \cos (2n_2 \pm n_1) t ,$$

where a and b represent the momentary values resp. of $2n_1(\beta_1 - \beta_3)$ and of $2n_2(\beta_2 - \beta_3)$.

In the extreme parallelopiped curves are described for which $\sin \varphi = 0$, so for which

$$2b \pm a = l\pi,$$

where l is an integer.

For this case we have, if we suppose l to be even,

$$\cos^{-1} \frac{z}{C} = 2 \cos^{-1} \frac{y}{B} \pm \cos^{-1} \frac{x}{A} .$$

RELATIONS BETWEEN 4 OF THE FREQUENCIES OF VIBRATION FOR WHICH $S = 4$.

§ 22. There are two of these relations to be discussed, namely:

$$(A) \quad n_1 + n_2 + n_3 - n_4 = \varrho.$$
$$(B) \quad n_1 + n_2 - n_3 - n_4 = \varrho.$$

After the preceding it will be clear that we have to take.

$$U = \tfrac{1}{2} \sum_{r=1}^{r=4} n_r^2 q_r^2 + H_4 (q_1, q_2, q_3, q_4),$$

$$T = \tfrac{1}{2} \sum_{r=1}^{r=4} \dot{q}_r^2 + \tfrac{1}{2} \sum_{r=1}^{r=4} \sum_{s=1}^{s=4} (P_{rr} \dot{q}_r^2 + 2P_{rs} \dot{q}_r \dot{q}_s),$$

where

$$P_{rs} = \tfrac{1}{2} a_{rs} q_1^2 + \tfrac{1}{2} b_{rs} q_2^2 + \tfrac{1}{2} c_{rs} q_3^2 + \tfrac{1}{2} d_{rs} q_4^2 + e_{rs} q_1 q_2 + f_{rs} q_1 q_3 +$$
$$+ g_{rs} q_1 q_4 + h_{rs} q_2 q_3 + k_{rs} q_2 q_4 + l_{rs} q_3 q_4.$$

We can again point out which terms in the different equations of motion are to be regarded as disturbing, and we can reduce them according to the method indicated in § 17.

The result of the reduction is that the disturbing terms of the second kind in the equations for q_1, q_2, q_3, and q_4 are the derivatives resp. to q_1, q_2, q_3, and q_4 of:

$(-n_1n_2l_{12} \mp n_1n_3k_{13} + n_1n_4h_{14} \mp n_2n_3g_{23} + n_2n_4f_{24} \pm n_3n_4e_{34} - p)\, q_2q_3q_4$

(p being the coefficient of a term $q_1q_2q_3q_4$ in H_1).

Of the $\mp$ and $\pm$ signs we must take the top one in the case of the relation (A) and the bottom one in the case of the relation (B).

We take as first approximation:

$$q_1 = \frac{\sqrt{\alpha_1}}{n_1} \cos (n_1t + 2n_1\beta_1),$$

$$q_2 = \frac{\sqrt{\alpha_2}}{n_2} \cos (n_2t + 2n_2\beta_2),$$

$$q_3 = \frac{\sqrt{\alpha_3}}{n_3} \cos (n_3t + 2n_3\beta_3),$$

$$q_4 = \frac{\sqrt{\alpha_4}}{n_1 + n_2 \pm n_3} \cos \{(n_1 + n_2 \pm n_3)t + 2(n_1 + n_2 \pm n_3)\beta_4\};\ \text{etc.}$$

We have then to take as function R:

$$-R = \chi_2 (\alpha_1, \alpha_2, \ldots \alpha_k) - \varrho' h^2 \alpha_4 + m_1 \sqrt{\alpha_1\alpha_2\alpha_3\alpha_4} \cos \varphi,$$

in which

$$\varphi = 2n_1 \beta_1 + 2n_2 \beta_2 \pm 2n_3 \beta_3 - 2 (n_1 + n_2 \pm n_3) \beta_4$$
$$= 2n_1 (\beta_1 - \beta_4) + 2n_2 (\beta_2 - \beta_4) \pm 2n_3 (\beta_3 - \beta_4).$$

§ 23. We can write down the equations which show the variability of the α's and β's with time and we find, as always in the case $S = 4$, that the coordinates $q_5, q_6 \ldots q_k$ feel the influence of the relation in their phase, but not in their amplitude.

We therefore occupy ourselves particularly with q_1, q_2, q_3, and q_4. The equations for $\dot{\alpha}_1$, $\dot{\alpha}_2$, $\dot{\alpha}_3$, and $\dot{\alpha}_4$ run:

$$\dot{\alpha}_1 = + 2n_1m_1 \sqrt{\alpha_1\alpha_2\alpha_3\alpha_4} \sin \varphi,$$

$$\dot{\alpha}_2 = + 2n_2m_1 \sqrt{\alpha_1\alpha_2\alpha_3\alpha_4} \sin \varphi,$$

$$\dot{\alpha}_3 = \pm 2n_3m_1 \sqrt{\alpha_1\alpha_2\alpha_3\alpha_4} \sin \varphi,$$

$$\dot{\alpha}_4 = - 2 (n_1 + n_2 \pm n_3)\, m_1 \sqrt{\alpha_1\alpha_2\alpha_3\alpha_4} \sin \varphi.$$

We deduce from this:

$$\frac{\dot{\alpha}_1}{n_1} = \frac{\dot{\alpha}_2}{n_2} = \pm \frac{\dot{\alpha}_3}{n_3} = - \frac{\dot{\alpha}_4}{n_1 + n_2 \pm n_3},$$

$$\dot{\alpha}_1 + \dot{\alpha}_2 + \dot{\alpha}_3 + \dot{\alpha}_4 = 0.$$

§ 24. *Case A.*

$$\frac{\alpha_1}{n_1} + \frac{\alpha_4}{n_1 + n_2 + n_3} = C_1h^2,\quad \frac{\alpha_2}{n_2} + \frac{\alpha_4}{n_1 + n_2 + n_3} = C_2h^2,\quad \frac{\alpha_3}{n_3} + \frac{\alpha_4}{n_1 + n_2 + n_3} = C_3h^2,$$

$$\frac{a_1}{n_1}-\frac{a_2}{n_2}=(C'_1-C'_2)h^2,\ \frac{a_1}{n_1}-\frac{a_3}{n_3}=(C'_1-C'_3)h^2,\ \frac{a_2}{n_2}-\frac{a_3}{n_3}=(C'_2-C_3)h^2,$$

where C'_1, C'_2, C'_3, represent positive constants.

If we put:

$$a_4=(n_1+n_2+n_3)\,\xi h^2.$$

we find

$$a_1=n_1\,(C_1-\xi)\,h^2,\ a_2=n_2\,(C_2-\xi)\,h^2,\ a_3=n_3\,(C_3-\xi)\,h^2.$$

The integral R = constant takes the form:

$$\sqrt{\xi\,(C_1-\xi)\,(C_2-\xi)\,(C_3-\xi)}\cos\varphi=p\xi^2+q\xi+r.$$

Case B.

$$\frac{a_1}{n_1}+\frac{a_4}{n_1+n_2-n_3}=C_1h^2,\ \frac{a_2}{n_2}+\frac{a_4}{n_1+n_2-n_3}=C_2h^2,\ \frac{a_3}{n_3}-\frac{a_4}{n_1+n_2-n_3}=C_3h^2,$$

$$\frac{a_1}{n_1}-\frac{a_2}{n_2}=(C_1-C_2)h^2,\ \frac{a_1}{n_1}+\frac{a_3}{n_3}=(C_1+C_3)h^2,\ \frac{a_2}{n_2}+\frac{a_3}{n_3}=(C_2+C_3)h^2,$$

where C_1, C_2, and C_3 are positive constants.

If we put:

$$a_4=(n_1+n_2-n_3)\,\xi h^2,$$

we find

$$a_1=n_1\,(C_1-\xi)h^2,\ a_2=n_2\,(C_2-\xi)h^2,\ a_3=n_3\,(C_3+\xi)h^2.$$

The integral R = *constant* takes the form:

$$\sqrt{\xi\,(C_1-\xi)\,(C_2-\xi)\,(C_3+\xi)}\cos\varphi=p\xi^2+q\xi+r.$$

It is clear that the problem is again reduced to quadratures and that the coordinates with the help of elliptic functions can be expressed in the time.

§ 25. The radius vector ξ varies periodically between two limits, lying in case A between zero and the smaller of the three quantities C_1, C_2, and C_3, in case B between zero and the smaller of C_1 and C_2.

The curves representing the relation between ξ and φ have here again the same form as for the case of the relation $n_2 = 3n_1$.

Thus as general forms of motion we have those where φ takes all values and those where φ moves backward and forward between two opposite values; the first we have by preference for great values of the residue of relation.

Furthermore there is again a special case where the amplitudes are constant, and $\sin\varphi$ remains 0; and another special case where such a form of movement is asymptotically approached.

§ 26. *Osculating curves.* The image point which is to represent the movement of the mechanism with 4 degrees of freedom, moves in a space R_4. The coordinates x, y, z, and u of the image point on a rectangular system of coordinates are at every moment equal to q_1, q_2, q_3, q_4. Its movement is then determined by:

$$x = \frac{\sqrt{a_1}}{n_1} \cos\,(n_1 t + 2 n_1 \beta_1)\,,$$

$$y = \frac{\sqrt{a_2}}{n_2} \cos\,(n_2 t + 2 n_2 \beta_2)\,,$$

$$z = \frac{\sqrt{a_3}}{n_3} \cos\,(n_3 t + 2 n_3 \beta_3)\,.$$

$$u = \frac{\sqrt{a_4}}{n_1 + n_2 \pm n_3} \cos \left\{(n_1 + n_2 \pm n_3)\, t + 2\,(n_1 + n_2 \pm n_3)\, \beta_4\right\}.$$

If we ascribe to the a's and β's their momentary values, then these equations represent the osculating curves for the indicated moment. The osculating curve we can call a LISSAJOUS curve.

The curve remains enclosed inside a fourdimensional parallelotope bounded by the spaces:

$$x = \pm \frac{\sqrt{a_1}}{n_1},\quad y = \pm \frac{\sqrt{a_2}}{n_2},\quad z = \pm \frac{\sqrt{a_3}}{n_3},\quad u = \pm \frac{\sqrt{a_4}}{n_1 + n_2 \pm n_3}\,.$$

By the variability of the a's the circumscribed parallelotope also changes; the vertices move backward and forward between two extreme positions along a wrung curve; this curve lies on a hyperellipsoid, whose axes lying along the axes of coordinates are proportional to $\frac{1}{n_1} : \frac{1}{n_2} : \frac{1}{n_3} : \frac{1}{n_1 + n_2 \pm n_3}$.

The form of the wrung LISSAJOUS curve in a definite parallelotope depends, as is found by a change of the origin of time, on the quantities

$$2 n_1 (\beta_1 - \beta_4), \quad 2 n_2 (\beta_2 - \beta_4), \quad 2 n_3 (\beta_3 - \beta_4).$$

The osculating curves described in the extreme parallelotopes have the property that

$$2 n_1 (\beta_1 - \beta_4) + 2 n_2 (\beta_2 - \beta_4) \pm 2 n_3 (\beta_3 - \beta_4) = l\pi.$$

For these curves the relation holds:

$$\cos^{-1} \frac{x}{A} + \cos^{-1} \frac{y}{B} \pm \cos^{-1} \frac{z}{C} = \cos^{-1} \frac{u}{D}\,,$$

when A, B, C, and D are written for the amplitudes and l is supposed even.

Mathematics. — *"On a system of conics in space."* By Mr. LUCIEN GODEAUX of Liege. (Communicated by Prof. P. H. SCHOUTE).

In this note I study a five times infinite system formed by conics in space, related to six connexes (point-plane) of the first order. This system of conics is in birational correspondence with the system of elements of space, each of which consists in a line and a plane passing through it. The conic corresponding to the combination of a line l and a plane π passing through it lies in the plane π, and a definite quadratic transformation of this plane into itself transforms the conic into the line l. It is in the definition of this quadratic correspondence that the given connexes enter.

1. Let be given to us in space two triplets of mutually independent connexes of the first order: Φ_1, Φ_2, Φ_3, Ψ_1, Ψ_2, Ψ_3. The equations of these connexes are respectively:

$$\begin{aligned}
\varphi_1(x,u) &\equiv x_1\,\varphi_{11}(u) + \;.\;.\;.\;.\; + x_4\,\varphi_{14}(u) = 0,\\
\varphi_2(x,u) &\equiv x_1\,\varphi_{21}(u) + \;.\;.\;.\;.\; + x_4\,\varphi_{24}(u) = 0,\\
\varphi_3(x,u) &\equiv x_1\,\varphi_{31}(u) + \;.\;.\;.\;.\;.\;.\;.\;. = 0,\\
\psi_1(x,u) &\equiv x_1\,\psi_{11}(u) + \;.\;.\;.\;.\; + x_4\,\psi_{14}(u) = 0,\\
\psi_2(x,u) &\equiv x_1\,\psi_{21}(u) + \;.\;.\;.\;.\; + x_4\,\psi_{24}(u) = 0,\\
\psi_3(x,u) &\equiv x_1\,\psi_{31}(u) + \;.\;.\;.\;.\;.\;.\;.\;. = 0,
\end{aligned}$$

point-coordinates being represented by (x_1, x_2, x_3, x_4) and tangential coordinates by (u_1, u_2, u_3, u_4).

Let m be the class of the first triplet of connexes and n that of the second, the functions $\varphi_{ik}(u)$ being of order m in the coordinates (u_1, u_2, u_3, u_4) and the functions $\Psi_{ik}(u)$ of order n.

Let us consider the general plane

$$u_x \equiv u_1 x_1 + u_2 x_2 + u_3 x_3 + u_4 x_4 = 0 \;.\;\;.\;\;.\;\;.\;\; (u)$$

The points which combined to this plane satisfy the equation of the connex Φ_1, form another plane meeting (u) in a line α_1. Likewise the connexes Φ_2, Φ_3, Ψ_1, Ψ_2, Ψ_3 determine in the plane (u) the lines α_2, α_3, β_1, β_2, β_3.

Let us imagine a quadratic transformation of the plane (u) in itself, transforming any line of that plane into a conic circumscribed to the triangle formed by the lines α_1, α_2, α_3. In order to define this transformation completely we suppose that to the lines β_1, β_2, β_3 correspond respectively the degenerated conics formed by the lines α_2 and α_3, α_3 and α_1, α_1 and α_2.

Let us try to form the equation of the conic ε corresponding to the line represented by the equations

$$a_x = 0,\ u_x = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (l)$$

and let us apply to the whole space the birational transformation (T), defined by

$$x_1 : x_2 : x_3 : x_4 = u_1 y_1 : u_2 y_2 : u_3 y_3 : y_4 - (u_1 y_1 + u_2 y_2 + u_3 y_3) . \qquad (T)$$

Then the plane $u_x = 0$ becomes the plane $y_4 = 0$, and the equation of the line α'_1 corresponding to α_1 runs

$$[\alpha'_1] = y_1(u_4 \varphi_{11} - u_1 \varphi_{14}) + y_2(u_4 \varphi_{12} - u_2 \varphi_{14}) + y_3(u_4 \varphi_{13} - u_3 \varphi_{14}) = 0. \quad (\alpha'_1).$$

The lines $\alpha_2, \alpha_3, \beta_1, \beta_2, \beta_3$ are transformed into the lines $\alpha'_2, \alpha'_3, \beta'_1, \beta'_2, \beta'_2$ characterized by analogous equations.

The equation of the line l' corresponding to l is

$$y_1 (u_4 a_1 - u_1 a_4) + y_2 (u_4 a_2 - u_2 a_4) + y_3 (u_4 a_3 - u_3 a_4) = 0. \qquad (l')$$

So the quadratic transformation of the plane (u) in itself becomes an analogous transformation of the plane $y_4 = 0$ in itself, any line

$$b_1 y_1 + b_2 y_2 + b_3 y_3 = 0 . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (b)$$

being transformed into a conic with the equation

$$(k_{11} b_1 + k_{12} b_2 + k_{13} b_3)[\alpha'_2][\alpha'_3] + \ldots . + (k_{31} b_1 + k_{32} b_2 + k_{33} b_3)[\alpha'_1][\alpha'_2] = 0. (1).$$

The undetermined parameters k may be eliminated by means of the remark, that if the line (b) coincides successively with $\beta'_1, \beta'_2, \beta'_3$, the corresponding conic Γ degenerates into the pairs of lines α'_2 and α'_3, α'_3 and α'_1, α'_1 and α'_2. So we easily find for the equation of the conic (ε') corresponding to the line l':

$$\Delta_{23} [\alpha'_2][\alpha'_3] + \Delta_{31} [\alpha'_3][\alpha'_1] + \Delta_{12} [\alpha'_1][\alpha'_2] = 0 , \quad . \qquad (2)$$

if $\Delta_{23}, \Delta_{31}, \Delta_{12}$ are defined by

$$\Delta_{23} = \begin{vmatrix} a_1 & a_2 & a_3 & a_4 \\ u_1 & u_2 & u_3 & u_4 \\ \mathfrak{v}_{21} & \mathfrak{v}_{22} & \mathfrak{v}_{23} & \mathfrak{v}_{24} \\ \mathfrak{v}_{31} & \mathfrak{v}_{32} & \mathfrak{v}_{33} & \mathfrak{v}_{34} \end{vmatrix} , \ \Delta_{31} \ \ldots , \ \Delta_{12} \ \ldots$$

Obviously the conic (ε') corresponds to the conic (d) obtained by transforming l in the plane u; so the equations of this conic will be found by applying to (2) the transformation (T^{-1}) represented by:

$$y_1 : y_2 : y_3 : y_4 = x_1 : x_2 : x_3 : u_x \quad . \quad . \quad . \quad . \quad . \qquad (T^{-1})$$

So after some reductions we find:

$$\left. \begin{array}{l} \Delta_{23}\, \mathfrak{v}_2\, \mathfrak{v}_3 + \Delta_{31}\, \mathfrak{v}_3\, \mathfrak{v}_1 + \Delta_{12}\, \mathfrak{v}_1\, \mathfrak{v}_2 = 0, \\ u_x = 0 \end{array} \right\} \quad . \quad . \quad . \quad . \qquad (\varepsilon)$$

which equations show that to the combination of a plane and a line in that plane corresponds a conic in that plane, and reversely, for we can pass from the equations (ε) to the equations:

$$u_x = 0,\quad a_x = 0.$$

So the conics ε form a five times infinite system E.

2. To a line l

$$a_x = 0,\ b_x = 0,\ \ldots\ldots\ldots\ldots \quad (l)$$

corresponds obviously a one time infinite system of conics of E; we now try to find the order of the surface S forming the locus of this system of conics.

Let us put

$$u_i = a_i + \lambda b_i \quad , \quad (i = 1, 2, 3, 4)$$

and apply this substitution to the first of the equations (ε). By subtracting in the determinants Δ_{23}, Δ_{31}, Δ_{12} the first row from the second, these determinants become of order $2m$ in λ; so we obtain an equation of order $2(m+n)$ in λ. By substituting in this equation for λ the value derived from

$$a_x + \lambda b_x = 0,$$

we find the equation of the locus S.

Remarking that any plane through l meets S in one conic only, we find the following theorem:

The conics corresponding to any line generate a surface S of order $2(m+n+1)$ passing $2(m+n)$ times through that line.

3. Let us now determine the locus of the lines in space, corresponding to conics of E passing through a given point P. Obviously this locus is a complex, which may be represented by $\boldsymbol{\Pi}$. As we started from connexes $\boldsymbol{\Phi}$, $\boldsymbol{\Psi}$ the equations of which are quite general, it will be sufficient, in order to determine the order of $\boldsymbol{\Pi}$, to find the number of lines in the plane $x_4 = 0$ passing through the point $x_2 = x_3 = x_4 = 0$, to which correspond conics of E passing through the point $P(x_1 = x_2 = x_3 = 0)$. This introduces the relations $u_1 = u_4 = 0$, $a_1 = 0$ into the equations (ε) of art. 1. Moreover we may suppose without any restriction that a_4 disappears too, for in the equations (ε) the parameters a_1, a_2, a_3, a_4 reduce themselves to three homogeneous parameters. So the condition that the planes

$$u_2 x_2 + u_3 x_3 = 0,\ a_2 x_2 + a_3 x_3 = 0$$

intersect according a line of the plane $x_4 = 0$ is

$$a_2 u_3 - a_3 u_2 = 0\ .\ \ldots\ldots\ldots\ldots \quad (3$$

Putting $k = \frac{u_2}{u_3}$ and taking into account the condition (3) the first equation (ε), in which the x represent the coordinates of the given point P, proves to be of order $2(m+n+1)$ in k, showing that Π is of order $2(m+n+1)$.

The lines, the corresponding conics of E of which pass through a given point P, form a complex Π of order $2(m+n+1)$.

4. Let us now consider a point P and a line p passing through it. Then the conics of E passing through P and lying in planes through p correspond to the lines of a congruence π contained in Π.

We immediately see that the congruence π is of the first order. For, in determining the number of lines of this congruence passing through any other point Q, it is evident that the plane (u) is completely determined by the conditions that it must contain line p and point Q. In this plane the lines to which correspond conics passing through P form a pencil, only one ray of which passes through Q. So we see too, that the line p is singular for the congruence.

Let $x_1 = x_2 = 0$ be the equations of the line p and $x_1 = x_2 = x_3 = 0$ the coordinates of the point P. Let us put $k = \frac{u_2}{u_1}$ and deduce the equations of a conic of E passing through P and lying in a plane through p; let

$$f(k, a) = 0, \; x_1 + kx_2 = 0,$$

be the resulting equations. Here $f = 0$, derived from the first equation (ε) of art. 1, is of order $2(m+n)+1$ in k and linear in (a_1, a_2, a_3, a_4).

Let us suppose $x_2 = 0$ and introduce moreover the supposition $a_1 = 0$ into the equation $f = 0$. The centre of the pencil formed by the lines of the plane

$$x_1 + kx_2 = 0 \quad , \quad \ldots \ldots \ldots \quad (4)$$

where $k \gtrless 0$, to which correspond conics passing through P, is determined by equation (4) and by

$$b_2\, x_2 + b_3\, x_3 = 0, \quad c_2\, x_2 + c_3\, x_3 = 0,$$

in connection with

$$f(k, b) = 0, \, f(k, c) = 0.$$

From this we conclude that the second singular line of π is a twisted curve of order $4(m+n+1)+1$ cutting the line p a number of $4(m+n+1)$ times (in the neighbourhood of $x_2 = 0$ this curve is determined by continuity).

The locus of the lines to which correspond conics of E passing through a given point P and lying in planes passing through a given line p through P is a congruence π of order unity and of class $4(m+n+1)+1$, *having the line p and a curve of order* $4(m+n+1)+1$ *for singular lines.*

We still remark that any two lines of the complex H, which do not belong to a same pencil lying in a plane through P, determine one and only one congruence π contained in H. So:

The complex H contains a net of congruences π.

5. It may happen that the line indicated by a_1 in art. 1 is not univocally determined for some particular positions of plane (u); this will be the case for the planes (u) satisfying the equations

$$\begin{matrix} \varphi_{i1}(u) & \varphi_{i2}(u) & \varphi_{i3}(u) & \varphi_{i4}(u) \\ u_1 & u_2 & u_3 & u_4 \end{matrix} = 0. \quad . \quad . \quad (5)$$

For under these conditions the plane defined by the connex Φ_1 coincides with the plane (u) and we can take for the line a_1 any line of this plane. In this case the quadratic transformation of the plane (u) in itself presents two degrees of indetermination; so we find: *To any line of a plane (u) given by the equations* (5) *correspond* ∞^2 *conics of the plane.*

The equations (5) are satisfied by $m^3 + m^2 + m + 1$ planes. Repeating the same reasoning for the connexes Φ_2, Φ_3 we find:

There are $3(m+1)(m^2+1)$ *planes with the property that to each line of the plane corresponds a double infinity of conics of the plane.*

Any plane of space generally contains a net of conics of E; if this plane satisfies the equations

$$\begin{matrix} \psi_{i1}(u) & \psi_{i2}(u) & \psi_{i3}(u) & \psi_{i4}(u) \\ u_1 & u_2 & u_3 & u_4 \end{matrix} = 0, \ (i = 1, 2, 3), \quad . \quad (6)$$

it is clear that any conic contained in it may be considered to correspond to an arbitrarily chosen line of the plane. So:

There are $3(n+1)(n^2+1)$ *planes with the property that to each line of the plane corresponds a net of conics in the plane, this net being the same for all the lines of the plane.*

Any plane satisfying either the equations (5) or the analogous ones for Φ_2, Φ_3, or the equations (6) is obviously principal for any complex H with respect to any point P of that plane.

Morlanwelz, December 1910.

Mathematics. — "*Continuous one-one transformations of surfaces in themselves*". (3rd Communication [1]). By Dr. L. E. J. Brouwer. (Communicated by Prof. D. J. Korteweg).

(Communicated in the meeting of December 24, 1910).

In the second communication several points of the argumentation were indicated, but in short. We shall now treat some auxiliary theorems, of which the proof is necessary for a complete development of the theory.

§ 1.

Definitions and lemmas.

On a surface we understand by a *finite continuum* a coherent set of points containing all its limiting points, and in which each fundamental series of points possesses a limiting point.

By a *continuum* we understand a coherent set of points containing all its limiting points and containing for every two of its points a finite continuum joining those two points.

A finite continuum determining only one rest region we shall call a *circular continuum*, if that rest region possesses for analysis situs the character of a rest region of a trema.

A continuum determining only one rest region, which is for analysis situs equivalent to the surface itself, we call a *paraboli continuum*[2].

A circular or a parabolic continuum together with a certain vicinity of it allows of a continuous one-one representation on a region of a Cartesian plane. There the circular continuum then lies entirel in a finite region, the parabolic continuum extends to the infinite Both determine in the Cartesian plane only one rest region and possess there a single circumference of *accessible* points, which lie in cyclic order for the circular continuum and in linear order for the parabolic continuum.

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[1] See these Proceedings Vol. XI, page 788, Vol. XII, p. 286. Compare also the abstract: "*Ueber eineindeutige, stetige Transformationen von Flächen in sich*" (Mathem. Annalen, Vol. 69, page 176), where the endresult of these researches is formulated.

[2] I do not maintain the term "open system of curves", which I used in the preceding communication (p. 291 sq.) for a nowhere dense circular or parabolic continuum.

A vector in the Cartesian plane being nowhere zero or infinite, of which the origin describes an arc of simple curve a and the endpoint as a continuous function of the origin another arc of simple curve b, starting in P and ending in Q, describes as integral of its infinitely small variations of direction a certain *total angular variation.*

If we substitute for b another arc of simple curve b' starting likewise in P and ending in Q, the two following theorems hold:

LEMMA 1. *If a has no point in common with $b+b'$, and if a is not separated from the infinite by $b+b'$, then the substitution of b' for b causes no change in the total angular variation of the vector.*

In that case we can namely construct a closed curve c containing a in its outer domain, $b+b'$ in its inner domain, and we can perform the modification of b into b' in a continuous way and entirely in the inner domain of c. The total angular variation of the vector can then on one hand undergo only continuous modifications, and on the other hand it can only vary by multiples of 2π; thus it remains unchanged.

LEMMA 2. *If b and b' form together a simple closed curve containing a in its inner domain, then by the substitution of b' for b the total angular variation of the vector increases or decreases by 2π, according to the positive sense of circuit of the closed curve corresponding to a movement of P to Q along b' or along b.*

If namely of a vector the endpoint describes a simple closed curve in a positive sense, whilst its origin describes as a continuous function of the endpoint a closed curve lying entirely inside that simple closed curve, we can by means of continuous modification, which does not change the total angular variation of the vector, transform the curve described by the endpoint into a circle, and reduce the curve described by the origin to the centre of that circle. Thus also before this modification the total angular variation is equal to 2π, from which lemma 2 immediately ensues.

§ 2.

The invariant point of the circular continuum.

We suppose a two-sided surface to be submitted with invariant indicatrix to a continuous one-one transformation in itself in such a way that a certain circular continuum q' passes thereby into itself.

We represent q' together with certain surroundings $\mathfrak{p}'$ uni-univalently and continuously on a region of a Cartesian plane, whereby they become respectively the images φ and ψ, and we suppose that φ' possesses no point invariant for the transformation.

We can then surround φ by a polygon $\mathfrak{P}$ approximating φ at a distance ε 1) and belonging entirely to ψ, in such a way that also the image of $\mathfrak{P}$ for the transformation lies entirely inside ψ, that in each point on or inside $\mathfrak{P}$ the length of the *transformation vector* (i.e. the vector joining the point with its image for the transformation) does not fall below a certain minimum b, and that each point of $\mathfrak{P}$ allows itself to be joined with φ by a path 2) $< \frac{1}{32} b$.

On $\mathfrak{P}$ we then choose the points $P_1, P_2, \ldots . P_n$, which have this order in the sense of a positive circuit, and possess the property that in each arc $P_k P_{k+1}$ (to these also belongs the arc $P_n P_1$) the distance of the endpoints lies between $\frac{1}{8} b$ and $\frac{3}{8} b$, and the distance of two arbitrary points does not exceed $\frac{3}{4} b$ 3). Let us now draw from each point P_k to φ a path $P_k R_k < \frac{1}{32} b$ lying inside $\mathfrak{P}$, then the arc of simple curve $R_k P_k P_{k+1} R_{k+1}$ *cannot cut* its image for the transformation $\boldsymbol{\rho}_k \boldsymbol{\pi}_k \boldsymbol{\pi}_{k+1} \boldsymbol{\rho}_{k+1}$.

The arcs $R_k P_k P_{k+1} R_{k+1}$ we shall call *skeleton arcs;* the arcs $\boldsymbol{\rho}_k \boldsymbol{\pi}_k \boldsymbol{\pi}_{k+1} \boldsymbol{\rho}_{k+1}$ *image skeleton arcs.*

If we represent by ϑ the total angular variation described by the transformation vector for a positive circuit of $\mathfrak{P}$, and by α_k the total angle described by a vector of which the origin runs along the skeleton arc $P_k P_{k+1}$, and the endpoint as a continuous function of the origin along the image skeleton arc $\boldsymbol{\pi}_k \boldsymbol{\pi}_{k+1}$, then we have

$$\vartheta = \Sigma \alpha_k .$$

By $\boldsymbol{\tau}_k$ we shall represent the point of the image skeleton arc $\boldsymbol{\pi}_k \boldsymbol{\rho}_k$, which is, if this arc does not cut $\mathfrak{P}$, identical to $\boldsymbol{\pi}_k$, and in the opposite case to its last point of intersection with $\mathfrak{P}$. If then β_k designs the total angular variation of a vector of which the origin runs along the skeleton arc $P_k P_{k+1}$ and the endpoint as a continuous function of the origin along the image skeleton arc $\boldsymbol{\tau}_k \boldsymbol{\tau}_{k+1}$, we have likewise

$$\vartheta = \Sigma \beta_k .$$

We now distinguish three cases:

1st. *On the circumference of* φ *the segments* $R_k R_{k+1}$ *and* $\boldsymbol{\rho}_k \boldsymbol{\rho}_{k+1}$

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1) Schoenflies, Bericht über die Mengenlehre II, p. 104.

2) i.e. "Weg" in the sense of Schoenflies.

3) Schoenflies, Bericht über die Mengenlehre II, p. 183.

lie outside each other (see fig. 1). Then we can join τ_k and τ_{k+1} by an arc of simple curve (drawn splintered in the figure), which lies inside $\mathfrak{P}$ as well as inside the domain enclosed between φ and the image skeleton arc $\varrho_k\tau_k\tau_{k+1}\varrho_{k+1}$, and which we shall call the *path* arc $\tau_k\tau_{k+1}$. This path arc together with the image skeleton arc $\tau_k\tau_{k+1}$ does not separate the skeleton arc P_kP_{k+1} from the infinite.

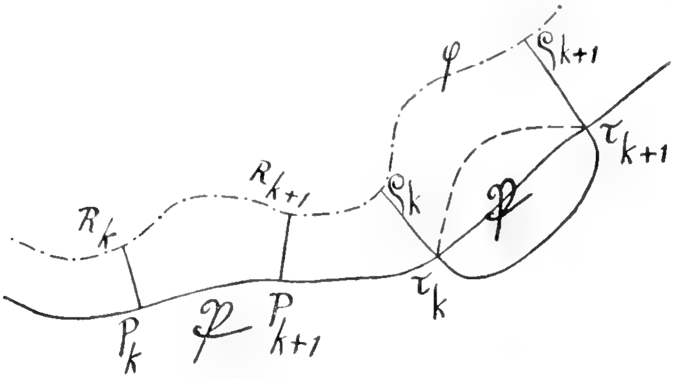

Fig 1.

So, if we represent by γ_k the total angle described by a vector of which the origin runs along the skeleton arc P_kP_{k+1}, and the end-point as a continuous function of the origin along the path arc $\tau_k\tau_{k+1}$, we have is this first case:

$$\beta_k = \gamma_k.$$

2nd. *On the circumference of* φ *the segment* R_kR_{k+1} *is a part of the segment* $\varrho_k\varrho_{k+1}$. Then too we can construct a path arc $\tau_k\tau_{k+1}$ (drawn splintered in fig. 2), which lies inside $\mathfrak{P}$ as well as inside the domain enclosed between φ and the image skeleton arc $\varrho_k\tau_k\tau_{k+1}\varrho_{k+1}$. But now this path arc forms with the image skeleton arc $\tau_k\tau_{k+1}$ a simple closed curve containing the skeleton arc P_kP_{k+1} in its inner domain, whilst its positive sense of circuit corresponds to a movement from τ_k to τ_{k+1} along the image skeleton arc $\tau_k\,\tau_{k+1}$.

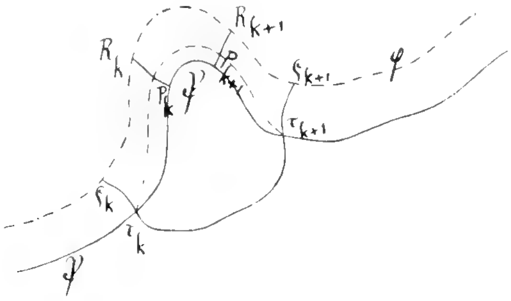

Fig. 2.

So we have in this second case, defining the angle γ_k in the same manner as in the first case:

$$\beta_k = \gamma_k + 2\pi.$$

3rd. *On the circumference of φ the segment $\varrho_k \varrho_{k+1}$ is a part of the segment $R_k R_{k+1}$* (see fig. 3). Then the image skeleton arc $\varrho_k \pi_k \pi_{k+1} \varrho_{k+1}$ lies entirely inside $\mathfrak{P}$, and we choose as path arc $\tau_k \tau_{k+1}$ the image skeleton arc $\tau_k \tau_{k+1}$ itself. Then we have in this third case, defining the angle γ_k in the same way as in the first and second cases:

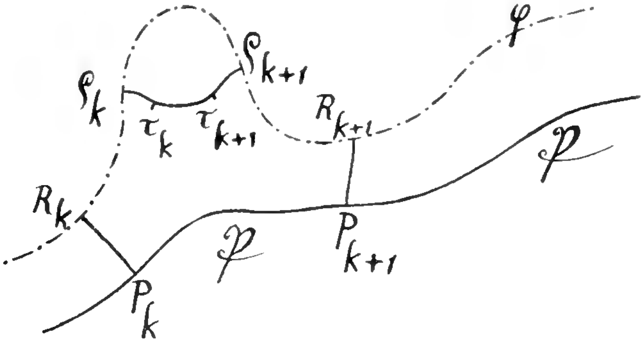

Fig. 3.

$$\beta_k = \gamma_k.$$

Now we can take $\Sigma \gamma_k$ as the total angular variation of a vector nowhere becoming zero, of which the origin describes $\mathfrak{P}$ in a positive sense and the endpoint as a continuous function of the origin a closed curve passing nowhere outside $\mathfrak{P}$, so that we have

$$\Sigma \gamma_k = 2\pi.$$

From this ensues in connection with the preceding formulae:

$$\Sigma \beta_k = 2n\pi,$$

where n represents a positive integer > 1.

Hence ϑ *cannot be equal to zero*, from which we conclude that the distribution of the transformation vectors must possess inside $\mathfrak{P}$ at least *one* singular point, i. o. w. that, contrary to the supposition at the commencement of this §, there must lie inside $\mathfrak{P}$ at least *one* point invariant for the transformation.

With this we have proved:

THEOREM 1. *For a continuous one-one transformation with invariant indicatrix of a two-sided surface in itself an invariant circular continuum contains at least one invariant point* [1]).

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[1]) Compare Mathem. Annalen, Vol. 69, p. 178; these Proceedings Vol. XII, p. 295.

§ 3.

The invariant point of the parabolic continuum.

We suppose a two-sided surface to be submitted with invariant indicatrix to a continuous one-one transformation in itself in such a way that by it a certain nowhere dense parabolic continuum φ' is transformed into itself.

We suppose that φ' possesses no point invariant for the transformation. Then its circumference cannot contain an invariant Schnitt either; for, this would be a circular continuum and therefore according to theorem 1 would give rise to an invariant point.

We represent φ' together with certain surroundings $\mathfrak{P}'$ uni-univalently and continuously on a region of a Cartesian plane whereby they become respectively the images φ and $\mathfrak{P}$. All the figures of the Cartesian plane to be constructed in the following and likewise their images for the transformation and their "counterimages" (i. e. their images for the inverse transformation) we suppose to lie in $\mathfrak{P}$. We suppose fartheron that for a positive circuit of the circumference of φ each accessible point precedes its image.

We surround φ by a fundamental series of polygonal lines $\mathfrak{P}_1$, $\mathfrak{P}_2$, $\mathfrak{P}_3$,... lying inside each other and approximating φ at indefinitely decreasing distances $\varepsilon_1, \varepsilon_2, \varepsilon_3, \ldots$, and we draw to an accessible point A lying on the circumference of φ a path w cutting each $\mathfrak{P}_k$ once and not more than once, and being $< 4\varepsilon_1$ [1]).

By a *circumference domain* of φ we understand such a segment of the linear type of order of its accessible points, as lies entirely outside its image segment, but for which each extension causes that property to be lost.

Let X and Y be two accessible points on the circumference of φ which are separated by A, whilst the order of succession XAY corresponds to a positive sense of circuit and between X and A as well as between A and Y there exist at least three circumference domains lying outside each other.

Let B be an accessible point of φ preceding X for a positive sense of circuit, possessing a finite distance p from the circumference segment XY, and belonging to the boundary of both regions determined by w between φ and $\mathfrak{P}_1$.

Let us understand by U an arbitrary accessible point of the

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[1]) Compare Schoenflies, Bericht über die Mengenlehre II, p. 127; L. E. J. Brouwer, "*Zur Analysis Situs*", Mathem. Annalen, Vol. 68, p. 428.

circumference of φ, whose distance from B does not exceed ε_1, then we suppose ε_1 to be so small that, independently of the choice of U, in all points whose distance from the circumference segment BU is $\leq 32\,\varepsilon_1$, the length of the transformation vector is $\geq 64\,\varepsilon_1$, whilst of an arc of simple curve $\leq 32\,\varepsilon_1$, running between two accessible points of the circumference of φ, if one of its endpoints belongs to the circumference segment BU, the image and the counterimage do not intersect each other.

Let C be an accessible point of φ lying beyond Y for a positive sense of circuit, and possessing from B a distance $< p$, and $< \frac{1}{4}\,\varepsilon_1$.

Let S_1 be the first positively directed circumference Schnitt not preceding B, past which up to A all accessible points of φ can be reached from the infinite along paths not meeting the straight line segment BC.

We then choose (see fig. 4) on the polygonal line $\mathfrak{P}_1$ an arc D_1E_1, in which the distance of the endpoints is $8\,\varepsilon_1$ and the distance of two arbitrary points is $< 16\,\varepsilon_1$, in such a way that from D_1 and E_1

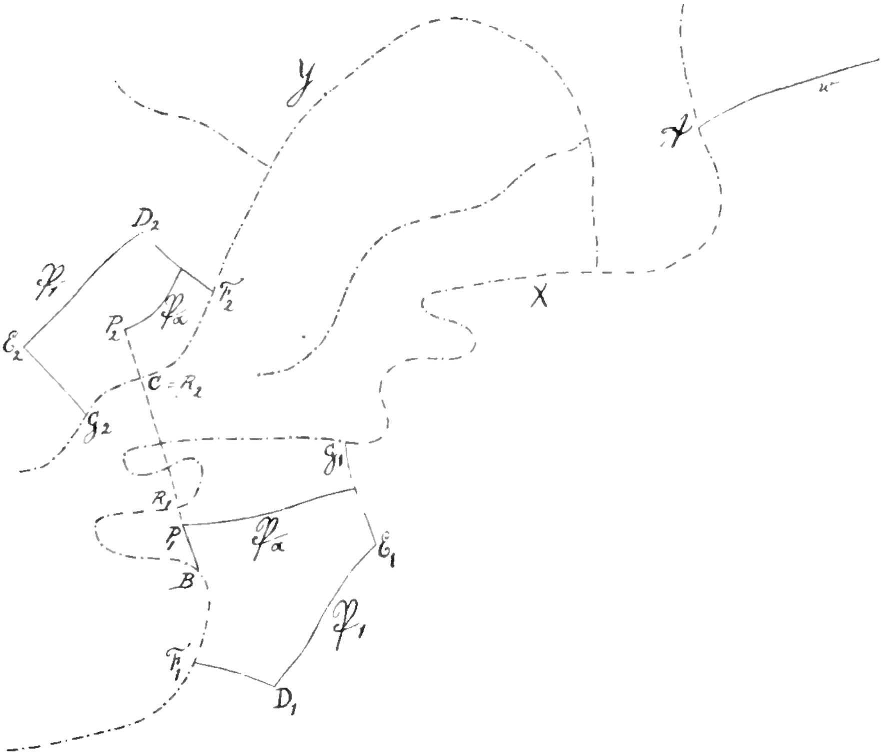

Fig. 4.

there can be laid to φ paths D_1F_1 and $E_1G_1 < 2\varepsilon_1$ not cutting the line segment BC and for $\alpha > m$ cutting each polygonal line $\mathfrak{P}_\alpha$ only once, whilst the Schnitt S_1 lies enclosed between these two paths. We may suppose ε_1 so small that not only the arc $F_1D_1E_1G_1$, but also its image *does not cut the path w.*

We now determine an approximating polygonal line $\mathfrak{P}_{\nu_1}$ ($\nu_1 > m$), possessing the following property:

If a part of the circumference segment F_1G_1 is separated from the infinite by the line segment BC, $\mathfrak{P}_{\nu_1}$ cuts the line segment BC between D_1F_1 and E_1G_1; then the last point of intersection, which BC has there with $\mathfrak{P}_{\nu_1}$, we represent by P_1;

in the opposite case $\mathfrak{P}_{\nu_1}$ cuts a path $< \frac{1}{8}\,\varepsilon_1$ leading to B, and not cutting D_1F_1 and E_1G_1; then its last point of intersection with that path we represent by P_1.

Let S_2 be the last negatively directed circumference Schnitt not lying beyond C possessing the property that between A and S_2 all accessible points of φ can be reached from the infinite along paths not meeting the straight line segment P_1C.

We then choose on the polygonal line $\mathfrak{P}_1$ an arc D_2E_2 in which the distance of the endpoints is $8\varepsilon_1$ and the distance of two arbitrary points is $< 16\varepsilon_1$, in such a way that from D_2 and E_2 there can be laid to φ paths D_2F_2 and $E_2G_2 < 2\varepsilon_1$ not cutting the line segment P_1C and for $\alpha > m$ cutting each polygonal line $\mathfrak{P}_\alpha$ only once, whilst the Schnitt S_2 lies enclosed between those two paths. We may suppose ε_1 so small that not only the arc $F_2D_2E_2G_2$, but also its image and its counterimage *do not cut the path w.*

We now determine an approximating polygonal line $\mathfrak{P}_{\nu_2}$ ($\nu_2 > m$) possessing the following property:

If a part of the circumference segment F_2G_2 is separated from the infinite by the line segment P_1C, $\mathfrak{P}_{\nu_2}$ cuts the line segment P_1C between D_2F_2 and E_2G_2; we then represent the first point of intersection, which P_1C has there with $\mathfrak{P}_{\nu_2}$, by P_2;

in the opposite case $\mathfrak{P}_{\nu_2}$ cuts a path $< \frac{1}{8}\,\varepsilon_1$ leading to C, and not cutting D_2F_2 and E_2G_2; we then represent its first point of intersection with that path by P_2.

Finally we impose on $\mathfrak{P}_{\nu_1}$ as well as on $\mathfrak{P}_{\nu_2}$ the condition that of their part contained between D_1F_1 and E_2G_2 the image as well as the counterimage lie inside $\mathfrak{P}_1$ and inside the image of $\mathfrak{P}_1$.

In the linesegment BC, eventually completed with the paths leading to B resp. to C that have been added to it, now lies an arc of simple curve $< \frac{1}{2}\varepsilon_1$ (drawn splintered fig. 4), joining P_1 and P_2, not cutting the arc of $\mathfrak{P}_{\nu_1}$ enclosed between P_1 and w neither the arc of $\mathfrak{P}_{\nu_2}$ enclosed between P_2 and w. On this arc of simple curve we represent the first resp. the last point of intersection with φ by R_1 resp. R_2.

By the *skeleton arc* $R_1P_1G_1$ we shall understand the arc of simple curve obtained by following from R_1 first the path R_1P_1, then $\mathfrak{P}_{\nu_1}$ up to its point of intersection with E_1G_1 and finally the path E_1G_1 from that point of intersection to G_1.

This skeleton arc $R_1P_1G_1$ does not meet its image skeleton arc $\varrho_1\pi_1\gamma_1$, which image skeleton arc cuts neither the path w nor the path E_1G_1, whilst the circumference segments R_1G_1 and $\varrho_1\gamma_1$ lie outside each other.

The arcs P_1G_1 and $\varrho_1\pi_1$ we join by an arc of simple curve K_1L_1 see fig. 5), belonging to an approximating polygonal line $\mathfrak{P}_{\tau_1}$ $(\tau_1 > \nu_1)$,

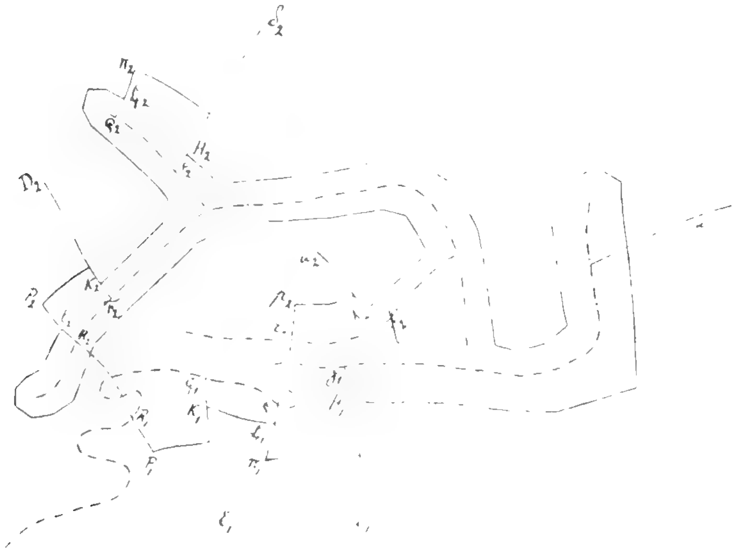

Fig. 5.

and abroad from its endpoints cutting neither the skeleton arcs $R_1P_1G_1$ and $\varrho_1\pi_1\gamma_1$, nor the paths w and E_1G_1.

The arc K_1L_1 we divide into such partial arcs, that on each of them the distance of the endpoints lies between $4\varepsilon_1$ and $12\varepsilon_1$ and the distance of two arbitrary points does not exceed $24\varepsilon_1$. From the endpoints of these partial arcs we draw to φ straight paths $< \frac{3}{2}\varepsilon_{\tau_1}$, among which we regard each pair of two successive ones, together with the partial arc of K_1L_1 connecting them, again as a skeleton arc.

By the *skeleton arc* $R_2P_2F_2$ we understand the arc of simple curve obtained by following from R_2 first the path R_2P_2, then recurring $\mathfrak{P}_{r_2}$ up to its point of intersection with D_2F_2 and finally following this path to F_2.

This skeleton arc $F_2P_2R_2$, its image $f_2p_2r_2$, and its counterimage $\varphi_2\pi_2\rho_2$ meet neither each other, nor the path w. Farthermore $\varphi_2\pi_2\rho_2$ cuts neither the path D_2F_2, nor its image d_2f_2, $f_2p_2r_2$ cuts neither the path D_2F_2, nor its counterimage $\delta_2\varphi_2$, and $F_2P_2R_2$ cuts neither the path $\delta_2\varphi_2$, nor the path d_2f_2.

The arcs P_2F_2 and $\rho_2\pi_2$ we join by an arc of simple curve K_2L_2, belonging to an approximating polygonal line $\mathfrak{P}_{\tau_2}$ ($\tau_2 > r_2$), and abroad from its endpoints cutting neither the skeleton arcs $R_2P_2F_2$, $\rho_2\pi_2\varphi_2$ and $r_2p_2f_2$, nor the paths w, D_2F_2, $\delta_2\varphi_2$ and d_2f_2, nor its own image k_2l_2.

The arcs $\pi_1\gamma_1$ and $\pi_2\varphi_2$ we join by an arc of simple curve H_1H_2, belonging to an approximating polygonal line $\mathfrak{P}_\tau$ ($\tau > r_1$ and $\tau > r_2$), and abroad from its endpoints cutting neither the paths E_1G_1 and D_2F_2, nor their images $\varepsilon_1\gamma_1$ and d_2f_2, nor the skeleton arcs $R_1P_1G_1$, $\rho_1\pi_1\gamma_1$, $\rho_2\pi_2\varphi_2$, $R_2P_2F_2$ and $r_2p_2f_2$, nor the joining arcs K_1L_1, K_2L_2 and k_2l_2.

Out of H_1H_2 and straight paths drawn from there to φ we finally construct skeleton arcs in the same way as above out of K_1L_1.

We have now built up a simple closed curve $P_1K_1L_1\pi_1H_1H_2\pi_2L_2K_2P_2R_2R_1P_1$, and, after addition of the image $\pi_1\rho_1r_2p_2$ of the arc $P_1R_1R_2P_2$ drawn splintered in the figure, a second simple closed curve $\pi_1H_1H_2\pi_2L_2K_2P_2l_2k_2p_2r_2\rho_1\pi_1$. These two closed curves have the arc $\pi_1H_1H_2\pi_2L_2K_2P_2$ in common, and this arc has for both closed curves the same inner side, so that it is *not separated from the infinite by the two completing arcs* $P_2R_2R_1P_1K_1L_1\pi_1$ and $P_2l_2k_2p_2r_2\rho_1\pi_1$.

The first closed curve we represent by $\mathfrak{C}$, and it is our aim to find the total angular variation of the transformation vector for a positive circuit of $\mathfrak{C}$.

To this end we can during the description of the arc $P_1K_1L_1\pi_1H_1H_2\pi_2$ substitute in the curve described by the endpoint of the transformation vector for each image skeleton arc a path arc according to the method of § 2, with the restriction that here we are always in the case 1st of that §. After that substitution the curve described by the vector endpoint passes nowhere outside $\mathfrak{C}$, whilst its first and its last point have remained the same, and the total angular variation of the vector has not changed.

We now come to the total angular variation of the transformation vector during the description of the arc $\pi_2 L_2 K_2 P_2$; on the ground of § 1 it can also be obtained by carrying first the origin of the vector along the arc $\pi_2 L_2 K_2 P_2$ and the endpoint as a continuous function of the origin along the arc $P_2 R_2 R_1 P_1 K_1 L_1 \pi_1$; and then, whilst the origin remains in P_2, carrying the endpoint still along the arc $\pi_1 \varrho_1 r_2 p_2$.

Finally we can obtain the total angular variation of the transformation vector during the description of the arc $P_2 R_2 R_1 P_1$ by carrying first the endpoint of the vector along $p_2 r_2 \varrho_1 \pi_1$ whilst the origin remains in P_2, and then the origin along $P_2 R_2 R_1 P_1$, whilst the endpoint remains in π_1.

So the total angular variation of the transformation vector for a positive circuit of $\mathfrak{C}$ is obtained by carrying first the origin of a nowhere vanishing vector along the arc $P_1 K_1 L_1 \pi_1 H_1 H_2 \pi_2$ and the endpoint as a continuous function of the origin along a certain curve nowhere passing outside $\mathfrak{C}$; then, whilst the origin runs along the arc $\pi_2 L_2 K_2 P_2$, carrying the endpoint along the arc $P_2 R_2 R_1 P_1 K_1 L_1 \pi_1$; and finally, whilst the endpoint remains in π_1, carrying the origin along the arc $P_2 R_2 R_1 P_1$.

In none of the three parts of this movement the endpoint of the vector has passed outside $\mathfrak{C}$, so that the total angular variation amounts to $+2\pi$, from which we conclude that, contrary to the supposition, the distribution of the transformation vectors must possess inside $\mathfrak{C}$ at least one singular point.

With this we have proved:

THEOREM 2. *For a continuous one-one transformation with invariant indicatrix of a two-sided surface in itself an invariant nowhere dense parabolic continuum contains at least one invariant point.*[1])

ERRATA.

In the 2nd communication on this subject, these Proceedings Vol. XII p. 289, in the note

for: Mathem. Annalen, Bd. 68.

read: Mathem. Annalen, Bd. 68, 69.

p. 297, l. 10—13 from top

for: furthermore, if no invariant point exists, we can arrange, that the just-mentioned series of images of ω, continued indefinitely on both sides, covers the whole Cartesian plane, i. o. w. we have proved:

read: i. o. w. we have proved:

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[1]) Compare Mathem. Annalen, Vol. 69, p. 178.

Physics. — *"On "osmotic temperatures" and the kinetic signification of the thermodynamic potential."* By Prof. Ph. Kohnstamm. (Communicated by Prof. J. D. van der Waals).

(Communicated in the meeting of December 24, 1910).

1. It may be presumed to be known, at least in Holland, how easily the laws of the diluted solutions are derived from the general differential equation of van der Waals for coexisting phases:

$$V_{21}\,dp = \frac{W_{21}}{T}\,dT + (x_2 - x_1)\left(\frac{\partial^2 \zeta}{\partial x_1^2}\right)_{pT} dx_1 \quad . \quad . \quad . \quad . \quad (1)$$

The law for the osmotic pressure alone does not immediately follow from the equation in the above form for the simple reason that it has been supposed in the derivation of this equation that the pressure in the two coexisting phases is equal. If we, however, return to the derivation of equation (1), we see at once the relation between this equation and the law of van 't Hoff. This derivation, namely, runs as follows. As in two coexisting phases 1 and 2 the thermodynamic potential e. g. of the first substance must be equal, and also in two other coexisting phases 1′ and 2′, the change of this thermodynamic potential between 1 and 1′, and 2 and 2′ must also be the same, and so if we take 1 and 1′ near each other, and represent the molecular thermodynamic potential of the first substance as usual by μ_1, the equation:

$$[d\mu_1]_1 = [d\mu_1]_2$$

holds.

Now from:

$$\mu_1 = \zeta - x\left(\frac{\partial \zeta}{dx}\right)_{pT}$$

follows:

$$d\mu_1 = d\zeta - \left(\frac{\partial \zeta}{\partial x}\right)_{pT} dx - x\,d\left(\frac{\partial \zeta}{\partial x}\right)_{pT}$$

And as

$$d\zeta = v\,dp - \eta\,dT + \left(\frac{\partial \zeta}{\partial x}\right)_{pT} dx$$

and

$$d\left(\frac{\partial \zeta}{\partial x}\right)_{pT} = \left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{pT} dx + \left(\frac{\partial^2 \zeta}{\partial x\,\partial p}\right)_{T} dp + \left(\frac{\partial^2 \zeta}{\partial x\,\partial T}\right)_{p} dT = \left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{pT} dx + \left(\frac{\partial v}{dx}\right)_{pT} dp - \left(\frac{\partial \eta}{\partial x}\right)_{pT} dT$$

we get:

$$d\mu_1 = \left\{ v - x\left(\frac{\partial v}{\partial x}\right)_{pT} \right\} dp - \left\{ \eta - x\left(\frac{\partial \eta}{\partial x}\right)_{pT} \right\} dT - x\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{pT} dx \;. \quad (2)$$

Equating of this expression for the first and the second phase, and joining the terms with dp, dT, and dx we get equation (1). When, however, we do not perform these operations, but keep to equation (2), we immediately find the law of VAN 'T HOFF. For we now reason as follows. The compressed dilute solution is in equilibrium with the solvent under normal pressure; so the thermodynamic potential of the solvent, which can freely move through the membrane, must be the same in the solution and in the pure solvent. And so the modification in the thermodynamic potential brought about on one hand by the increase of pressure, on the other by the addition of the dissolved substance, must be equal to zero, and so, as $dT = 0$:

$$\left\{ v - x\left(\frac{\partial v}{\partial x}\right)_{pT} \right\} dp = x\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{pT} dx$$

follows from (2).

Now for an exceedingly dilute solution $x\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{pT} = \frac{RT}{1-x}$; in the first member of the equation we can neglect the term with x, and we need not make a difference between the v of the solution and that of the solvent, and so we get:

$$v\, dp = \frac{RT}{1-x}\, dx \;^{1)},$$

the law of VAN 'T HOFF.

2 Now when we consider the osmotic phenomenon, the thought of introducing the idea "osmotic temperature" as analogy of the osmotic pressure, naturally suggests itself, and this has repeatedly been done [2]). The reasoning is then as follows. The equilibrium through the semipermeable membrane is disturbed when on one side a substance is dissolved, because then the number of particles of the solvent per unit of volume decreases. So if we want to reach a state in which an equal number of particles move from the left towards the right and from the right towards the left we must either raise the pressure of the solution, in consequence of which more solvent molecules are forced out, or its temperature, so that the number of outgoing molecules will be increased by the greater velocity. Now the increase of temperature which must be given to the solution

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[1]) Cf. Théorie Moléculaire § 18

[2]) Cf. e. g. VAN LAAR, These Proc. IX, p. 61.

above the solvent to bring about that an equal number of particles enter and leave through the membrane, is called the "osmotic temperature" of this solution. Now the supposition naturally suggests itself that this state is reached when the thermodynamic potential of the substance passing through the membrane has again become equal in the solution and the solvent. This thesis would undoubtedly be correct, if the considerations concerning the kinetic signification of the thermodynamic potential which I gave in These Proc. April **1905**, were perfectly true. There I tried to demonstrate that the physical meaning of the thermodynamic potential of an homogeneous phase on which no external forces act is nothing but the number of molecules which per second reaches a wall, which is placed in the middle of this homogeneous phase, when the wall does not attract the molecules, and is thick with respect to their sphere of action. I expressed this definition by the formula:

$$M\mu = F(N) \quad C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which N is the number of molecules in question, and C a constant. It is clear that what has been said above follows from this formula: for the numbers of molecules which leave solution and solvent through the membrane, are then entirely determined by the thermodynamic potential.

If now, however, on this ground, we try to determine from equation (2), what the "osmotic temperature" will be for a certain solution, we come to an absurdity. For, again neglecting the terms with x, we get for the osmotic temperature at constant pressure:

$$\eta\, dT = RT\, dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

So this would imply that we could determine the total amount of entropy of the solvent through the experimental determination of $\frac{dT}{dx}$. And this now is an absurdity. For when we reason purely thermodynamically and so define the entropy by $d\eta = \frac{dQ}{T}$ — and we have used no other definition of the entropy in deriving equation (4), — the entropy has no definite value, but an indefinite, and undefinable additive constant occurs in it; only differences of entropy have a definite value. ¹)

3. It is not difficult to point out the error in the reasoning which has led us to this absurdity. We have imposed the condition that

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¹) Only by starting from another, kinetic definition of the entropy, we can assign a definite value to the entropy in a definite system of units. Cf. These Proc. XIII p. 705, seq.

the thermodynamic potential of the substance passing through the membrane should be the same on the two sides, and we were not justified in this. For it is indeed true that in states of *equilibrium* the thermodynamic potential of a component is the same in every phase, but here we have no state of equilibrium, because there continues to exist a difference of temperature between solution and solvent, and so a current of heat. It is just by this that the "osmotic temperature" is distinguished from the osmotic pressure, that the latter gives a state of equilibrium, though under special restricting conditions (the membrane).

Yet it is clear that it must be possible to reach a stationary state by rise of temperature in the way indicated; but the condition on which this takes place, must not defined in this way that the thermodynamic potentials become equal. As it is self-evident that this condition will have to be that the total number of particles passing through the membrane is zero, it follows further that formula (3) cannot be maintained, and will have to be replaced by a relation of the form:

$$N = F(\mu, T). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Other quantities than the temperature (and constants) cannot occur in this relation, because the properties of the thermodynamic potential in equilibrium, i.e. at one definite temperature in all phases, require that equation (5) reduces to (3) for constant temperature. It is now neccessary for both problems to define the form of equation (5) closer. It is clear that a purely thermodynamic reasoning is not adequate to do so, because the problem we want to solve, falls outside thermodynamics as relating to states of non-equilibrium. Thermodynamics can only give indications about the solution, however valuable these may be; the solution itself can only be obtained by kinetic means. One of these indications is this that the function of equation (5) will have to be of such a nature that the condition $N_1 = N_2$ does not lead to the absurd result (4). Now this absurdity already disappears when equation (5) is brought into the form:

$$N = C\,\frac{\mu}{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

in which the factor R is required by the consideration that N is a number of molecules that reaches a certain surface in the unit of time. As μ is of the dimension of an energy, also the denominator will have to be of this dimension, the factor C being in a certain relation with the unit of time and surface. If we draw up the condition of equilibrium by the aid of (6), it runs of course as follows:

$$\left(\frac{\partial \frac{\mu}{RT}}{\partial x}\right)_{p,T} dx + \left(\frac{\partial \frac{\mu}{RT}}{\partial T}\right)_{p,x} dT = 0$$

or

$$\frac{x\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{p,T}}{RT} dx = \frac{T\left(\frac{\partial \mu}{\partial T}\right)_{p,x} - \mu}{RT^2} dT$$

or

$$\frac{dx}{1-x} = \frac{-T\eta + xT\left(\frac{\partial \eta}{\partial x}\right)_{p,T} - \varepsilon + T\eta - pv + x\left(\frac{\partial \varepsilon}{\partial x}\right)_{p,T} - xT\left(\frac{\partial \eta}{\partial x}\right)_{p,T} + px\left(\frac{\partial v}{\partial x}\right)_{p,T}}{RT^2} dT$$

in which it is just the terms with η that are cancelled. Now it appears, however, that also this expression is still too simple, for now ε is found in the result, in which also an indefinite constant occurs in consequence of the potential energy. So instead (6) we must have an expression of the form:

$$N = Ce^{\frac{\mu - f(T)}{RT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which $f(T)$ is either a constant, or a function of T which is still further to be determined. But let us now still put the condition that N becomes equal to zero for very great volumes, and always remains positive in other cases. Then we see that (7) cannot satisfy this, because for very great volume the entropy becomes infinite and so the thermodynamic potential becomes negative infinite. This consideration requires a dependence of the form:

$$N = Ce^{\frac{\mu - f(T)}{RT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

in which it does not make any difference whether we take C as a constant, or as a function of T, as long as $f(T)$ remains quite arbitrary.

4. Further than equation (8) thermodynamic theory cannot go. So we must now try if we cannot confirm the up to now only plausible result in a kinetic way, and get a further insight into the nature of $f(T)$. By the way indicated by VAN DER WAALS SR. in his communication on the kinetic meaning of the thermodynamic potential [1]) this is easily obtained. We need only modify the train of reasoning in so far, that we do not direct our attention to the equality of the number of molecules that passes from the liquid into

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[1]) Verslagen Kon. Akademie III, 205—219.

the gas phase, and vice versa, but independent of the second phase determine the number of particles which may detach themselves from the surrounding homogeneous phase, i.e. which are able entirely to overcome the power of attraction of the phase in which they are found, and so can reach a space where if no external forces are active the potential energy is maximum and the kinetic pressure may therefore be put zero.[1]

However, a few objections may be advanced to the method followed l. c., particularly with respect to the way in which the loss of energy is calculated when a molecule leaves the homogeneous phase. I am indebted to Prof. VAN DER WAALS Jr. for the following proof, in which these difficulties are evaded.

Let N' be the number of molecules of one gram molecule, $\frac{a}{v}$ its potential energy, then the potential energy which one molecule loses when it is removed from the phase to a place where the potential is zero, is $\frac{2a}{N'v}$. The influence of the collisions which one molecule meets with from another, can be reduced to a pressure on the distance sphere, as this is frequently done in the derivation of the equation of state by the virial method. This pressure, which we shall call P, is equal to $p+\frac{a}{v^2}$ or $\frac{MRT}{v-b}$.

If we want to determine the chance that a molecule escapes from the phase through the capillary layer, we shall have to take this pressure into account. For it is not constant through the capillary layer, but will gradually decrease if we traverse the capillary layer from the liquid in the direction towards the vapour.

If we choose the Z-axis normal to the capillary layer and if we think σ (the radius of the distance sphere) so small compared with the thickness of the capillary layer that over the distance 2σ we may consider the pressure P as a linear function of z, the force with which a molecule is pressed outside by the pressure P will be equal to $-\frac{4}{3}\pi\sigma^3\frac{dP}{dz}$. So the total work which is exerted by P on

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[1] Prof. VAN DER WAALS Jr. points out to me that these conditions need not always be satisfied in the neighbourhood of a wall as was mentioned in my previous paper, which is easily seen if we think of liquid phases in the neighbourhood of their critical temperature. So if we want in general to define the thermodynamic potential kinetically in a definite case only by means of properties of this phase itself, and not of coexisting phases — and this seems desirable to me in many respects — we must replace the definition by means of a non-attracting wall by the purely mathematic one given in the text.

an outgoing molecule is:

$$\frac{4\pi}{3}\rho^3\int\frac{dP}{dz}dz=\frac{4}{3}\pi\rho^3(P_l-P_g)=\frac{2b_\infty}{N}(P_l-P_g)$$

So when a molecule penetrates into the capillary layer in the direction from the liquid to the gas, it can traverse it entirely only when the z-component (u) of the velocity is so great that:

$$\tfrac{1}{2}m\,u^2>\left(\frac{2a}{Nv}\right)_l-\left(\frac{2a}{Nv}\right)_g-\frac{2b_\infty}{N}(P_l-P_g).$$

Let us call the smallest value of u which satisfies this u_m, we then find the number of particles which escapes from the liquid per second as follows: Let n be the number of particles per cm^3., so $n=\frac{N'}{v}$ ($v=$ the volume of 1 gram molecule), then the number that has a velocity component u in the z-direction is $\frac{n}{\sqrt{\pi}}e^{-\frac{u^2}{\alpha^2}}d\frac{u}{\alpha}$, and the number which passes through an area of 1 cm^2 with that velocity:

$$\frac{n}{\sqrt{\pi}}ue^{-\frac{u^2}{\alpha^2}}d\frac{u}{\alpha}$$

So the number that passes from liquid to vapour is:

$$\frac{n\alpha}{\sqrt{\pi}}\int_{u=u_m}^{u=\infty}\frac{u}{\alpha}e^{-\frac{u^2}{\alpha^2}}d\frac{u}{\alpha}=\frac{n\alpha}{2\sqrt{\pi}}e^{-\frac{u^2_m}{\alpha^2}}$$

If we have to deal not with a simple substance, but with a mixture of $(1-x)$ molecules 1st kind and x molecules 2nd kind, and if we want to ascertain the equilibrium for molecules 1st kind, we get, as is easy to see, the same expression, in which, however, $n=\frac{N'(1-x)}{v}$ ($v=$ the volume of 1 gram molecule of the mixture and:

$$\tfrac{1}{2}m_1u^2_m=\left[\frac{2\{(1-x)a_1+xa_{12}\}}{N'v}\right]_l-\left[\frac{2\{(1-x)a_1+xa_{12}\}}{N'v}\right]_g$$
$$-\frac{2RT}{N'}\left(\left[\frac{b_1(1-x)+b_{12}x}{v-b}\right]_l-\left[\frac{b_1(1-x)+b_{12}x}{v-b}\right]_g\right)$$

The expressions $\frac{(1-x)RT}{v-b}$ and $\frac{xRT}{v-b}$ here represent the partial pressures exerted resp. by molecules of the 1st and of the 2nd kind on the distance spheres round those of the 1st kind. The available spaces being different for the molecules of different kinds, the denominators $v-b$ should strictly speaking also have different values. As it is here, however, only our purpose to examine what function μ is of X, we may disregard these differences.

So if we take into consideration that $^1/_2 m_1 N' u^2 = MRT$, the number of particles which passes from the liquid to a space where the potential energy is maximum and the kinetic pressure $=0$, amounts to:

$$N = \frac{N'(1-x)\alpha}{v\, 2\sqrt{\pi}}\, e^{\frac{-2\left\{\frac{(1-x)a_1+xa_{12}}{v}\right\}+2RT\left\{\frac{b_1(1-x)+b_{12}x}{v-b}\right\}}{RT}}$$

or

$$N = C\sqrt{T}\, e^{\frac{-2\left\{\frac{(1-x)a_1+a_{12}x}{v}\right\}+2RT\left\{\frac{b_1(1-x)+b_{12}x}{v-b}\right\}+RT\,l\,\frac{1-x}{v}}{RT}} \qquad (9)$$

where $C = \sqrt{\dfrac{RN'}{2\pi m}}$.

5. It remains to show that the expression in the exponent agrees with $\mu - f(T)$ of equation (8).

Now, if we leave the pure functions of the temperature out of consideration, the thermodynamic potential becomes:

$$pv - RT\,l\,(v-b) - \frac{a_x}{V} - x\left\{\frac{RT\frac{db}{dx}}{v-b_x} - \frac{\frac{da}{dx}}{v}\right\} + RT\,l\,(1-x) \quad . \quad . \quad (10)$$

if b may be considered as a constant. This is, of course not the case in the liquid state, and accordingly we can only expect to obtain agreement between (9) and (10), when we neglect terms with higher powers of $\dfrac{b}{v}$.

If we write $pv = RT\dfrac{v}{v-b} - \dfrac{a}{v}$, the terms with a from equation (10) become:

$$-\frac{2a - x\frac{da}{dx}}{v} = -\frac{2a_1(1-x)+2a_{12}x}{v}$$

and so these terms perfectly agree with those of (9).

With neglect of the higher powers of $\dfrac{b}{v}$, the terms with b from equation (10) can be reduced as follows:

$$-l(v-b)-\frac{x\frac{db}{dx}}{v-b}+\frac{v}{v-b}=-l(v)-l\left(1-\frac{b}{v}\right)-\frac{x\frac{db}{dx}}{v-b}+\frac{v}{v-b}=$$

$$=-l(v)+\frac{b}{v}-\frac{x\,db}{v\,dx}\left(1+\frac{b}{v}\right)+1+\frac{b}{v}=-l(v)+1+\frac{2b-x\frac{db}{dx}}{v}=$$

$$=1-l(v)+\frac{2b_1(1-x)+2b_{12}x}{v}.$$

So these terms too perfectly agree with those of equation (9), provided the higher powers of $\frac{b}{v}$ are neglected. So the $f'(T)$ of equation (8) should be chosen so that the functions only dependent on temperature disappear from the thermodynamic potential, and the whole expression is multiplied by $\sqrt{T}$. So the two methods, the kinetic and the thermodynamic method supplement each other. Thermodynamically it can be shown that the quantity which occurs in the exponent of equation (8), must necessarily be the thermodynamic potential, at least as regards its dependence on v and x; but concerning its pure functions of the temperature thermodynamics cannot give a decision. On the other hand the kinetic theory is adequate to show, that we must get an equation of the form of equation (8) for N, and it can determine the $f'(T)$. It can, however, show with only a very rough approximation — until a proper expansion into series for b is known — that the occurring function of the volume and the concentration is the same as that which occurs in the thermodynamic potential. If these two methods are combined, we may, in my opinion, conclude with certainty, that the number of particles under investigation is really represented by the formula:

$$N=C\sqrt{T}\,e^{\frac{\mu'}{RT}} \qquad (11)$$

in which μ' represents the thermodynamic potential without its functions only dependent on the temperature.

6. Now it is easy to draw up the equation for the "osmotic temperature" by means of formula (11). A stationary state will, namely, set in when the number of molecules going to pass through the membrane on one side of it has increased by rise of temperature as much as it has decreased by the addition of the dissolved substance, or in other words, when:

$$\left(\frac{\partial N}{\partial x}\right)_{p,T} dx + \left(\frac{\partial N}{\partial T}\right)_{p,x} dT = 0 \quad . \quad . \quad . \quad . \qquad (12)$$

If we write $\mu' = \mu + F(T)$, in which now:

$$F(T) = -\int_0^T c_{v\infty}\, dT - E + T\int_1^T \frac{c_{v\infty}}{T}\, dT + TH$$

and in which μ is the ordinary thermodynamic potential, then

$$-\left(\frac{\partial \mu}{\partial x}\right)_{p.T} dx = \frac{dT}{T}\left\{T\left(\frac{\partial \mu}{\partial T}\right)_{p,x} + TF'(T) - \mu - F(T) + \frac{RT}{2}\right\}.$$

follows immediately from equation 11 and 12, when the differentiations have been carried out.

And with the values for $\left(\frac{\partial \mu}{\partial x}\right)_{p,T}$ and $\left(\frac{\partial \mu}{\partial T}\right)_{p,x}$ from equation (2)

$$x\left(\frac{\partial^2 \zeta}{\partial x^2}\right)_{p,T} dx = \frac{dT}{T}\left\{TF'(T) - \varepsilon - pv - F(T) + \frac{RT}{2}\right\} \quad . \qquad (13)$$

when we may consider the terms with x as small.

Then with $\varepsilon = -\frac{a}{v} + \int_0^T c_{v\infty}\, dT + E$ and the above-mentioned value of $F(T)$ the righthand member becomes:

$$\frac{dT}{T}\left\{\frac{a}{v} - pv + \frac{RT}{2}\right\}$$

Now at low temperature pv may be neglected by the side of $\frac{a}{v}$, and for the latter expression we may write $\frac{RTv}{v-b}$. On the supposition already introduced by us that x is small, $\left(\frac{\partial^3 \zeta}{dx^2}\right)_{p.T}$ passes into $\frac{RT}{x(1-x)}$, so that finally the differential equation of the "osmotic temperature" becomes:

$$\frac{dx}{1-x} = \frac{dT}{T}\left\{\frac{v}{v-b} + \frac{1}{2}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (14)$$

It is evident that the second member is positive, and this result was, of course, already certain beforehand.

7. In connection with this result a single remark may be allowed me. We might think that the experimental determination of the "osmotic temperature" would give a new means for the determination of the quantity b in the liquid state; this is, however, not the case. This

appears when we do not wait till (13) to introduce the simplification that pv may be neglected by the side of $\frac{a}{v}$, but introduce it immediately in (11). If we write this equation in the form:

$$l(N) = lC + {}^1/_2\, lT + \frac{\mu'}{RT}$$

we find as condition for the stationary state:

$$\left(\frac{\partial \frac{\mu'}{RT}}{\partial x}\right)_{p,T} dx = \frac{dT}{2T} + \left(\frac{\partial \frac{\mu'}{RT}}{\partial T}\right)_{p,x} dT \quad . \quad . \quad . \quad (15)$$

Now on the mentioned supposition, and neglecting again the terms with x, we have:

$$\frac{\mu'}{RT} = \frac{-\frac{a}{v}}{RT} - l(v-b) + l(1-x) = -\frac{v}{v-b} - l(v-b) + l(1-x)$$

and so:

$$\left(\frac{\partial \frac{\mu'}{RT}}{dx}\right)_{p,T} = -\frac{dx}{1-x}\,,\quad \left(\frac{\partial \frac{\mu'}{RT}}{\partial T}\right)_{x,p=0} = \frac{2b-v}{(v-b)^2}\left(\frac{\partial v}{\partial T}\right)_{p=0} . \quad (16)$$

$\left(\frac{\partial v}{\partial T}\right)_{p=0}$ we find from the equation:

$$\frac{a}{v^2} = \frac{RT}{v-b}$$

by differentiation; the result becomes after some reduction:

$$\left(\frac{\partial v}{\partial T}\right)_{p=0} = \frac{v(v-b)}{T(2b-v)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

If we substitute this result and that of (16) into (15), we get again (14). So we see now that (14) does not give an independent determination of $\frac{v}{v-b}$, but that we can just as well determine this quantity from (17). And as the quantities occurring in (17) can undoubtedly be determined experimentally with much greater accuracy than the "osmotic temperature", there is no reason to expect that equation (14) will be able to give us any new information about the b in the liquid state. And in my opinion this obviates every reason, at least for the present, to try and conquer the undoubtedly very considerable difficulties which will confront us in an experimental investigation of "osmotic temperatures".

Physics. — "*Thermodynamic potential and velocities of reaction.*" By Prof. Ph. Kohnstamm and Dr. F. E. C. Scheffer. (Communicated by Prof. J. D. van der Waals).

(Communicated in the meeting of December 24, 1910).

§ 1. In the preceeding communication one of us has shown that the number of molecules of a substance in a homogeneous phase which is able to escape from the attraction of this phase in the unity of time is indicated by the expression:

$$N = C\sqrt{T}\,e^{\frac{\mu'}{RT}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which μ' represents the thermodynamic potential of this substance in that phase deprived of its mere temperature functions, and R the molecular gas constant. This formula was applied there to find the condition of the stationary state, in which an equal number of particles enter a solution as leave it through a semi-permeable membrane, but another use of this formula is conceivable. We may, namely, put the question: When there is no equilibrium of exchange between solution and solvent through the membrane, how many more particles per unit of time will then leave the solution than enter it, or in other words how great will be the velocity in a certain state with which the whole system tends to reach equilibrium? It will be expected that in the case mentioned the velocity may be represented by the difference between two expressions of the form (1), the former of which represents the number of particles which leaves the solution, and the second the number of molecules that leaves the solvent, and so enters the solution. We then get for this velocity the expression:

$$N = C\left\{\sqrt{T_1}\,e^{\frac{\mu'_1}{RT_1}} - \sqrt{T_2}\,e^{\frac{\mu'_2}{RT_2}}\right\}.$$

Such a formula would, of course, have to hold for all analogous cases; e.g. for that of the osmotic pressure and for the evaporation of liquids. These velocities, however, do not act a very prominent rôle in physics, and application of the formula to these cases does not seem to open new vistas, the less so as there would hardly be any experimental material to test them by. The problem of the velocities of reaction, on the contrary, plays a most important part in chemistry, and in this department there is a rich experimental material at our disposal. When we now consider that with these chemical velocities also a great number of particles leaves the reacting mixture with formation of new substances, the question naturally suggests itself whether the expression found will not be able to throw some new light on this region.

So we shall have to investigate whether the velocity of reaction can be expressed in the following form:

$$-\frac{dc}{dt} = C\left(e^{\frac{\mu_{\mathrm{I}}+F_1}{RT}} - e^{\frac{\mu_{\mathrm{II}}+F_2}{RT}}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which μ_{I} and μ_{II} are the sum of the molecular thermodynamic potentials resp. for the disappearing and forming systems, and F_1 and F_2 functions of the temperature, and further of constants which refer to the reacting substances or perhaps to the intermediate states occurring in the reaction [1]). The two functions F_1 and F_2 have the dimension of an energy, and the value of the constant C accounts for the choice of our unity of concentration and time. For its dimension is c/t, and accordingly may be taken equal for the two partial reactions.

§ 2. Now in the first phase we shall show that both for rarefied gases and for dilute solutions equation (2) leads to the well-known expression for the law of mass-action. If in (2) we substitute the value of μ for a mixture of rarefied gases:

$$\mu_{\mathrm{I}} = \Sigma \mathbf{r}_{\mathrm{I}}\, \varepsilon_{0_{\mathrm{I}}} - T \Sigma \mathbf{r}_{\mathrm{I}}\, \eta_{0_{\mathrm{I}}} + \Sigma \mathbf{r}_{\mathrm{I}} \int c_{v_{\mathrm{I}}}\, dT - T\, \Sigma \mathbf{r}_{\mathrm{I}} \int \frac{c_{v_{\mathrm{I}}}}{T}\, dT +$$
$$+ RT\, \Sigma \mathbf{r}_{\mathrm{I}}\, ln\, c_{\mathrm{I}} + RT\, \Sigma \mathbf{r}_{\mathrm{I}}$$

and

$$\mu_{\mathrm{II}} = \Sigma \mathbf{r}_{\mathrm{II}}\, \varepsilon_{0_{\mathrm{II}}} - T \Sigma \mathbf{r}_{\mathrm{II}}\, \eta_{0_{\mathrm{II}}} + \Sigma \mathbf{r}_{\mathrm{II}} \int c_{v_{\mathrm{II}}}\, dT - T\, \Sigma \mathbf{r}_{\mathrm{II}} \int \frac{c_{v_{\mathrm{II}}}}{T}\, dT +$$
$$+ RT\, \Sigma \mathbf{r}_{\mathrm{II}}\, ln\, c_{\mathrm{II}} + RT\, \Sigma \mathbf{r}_{\mathrm{II}}$$

we get:

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[1]) According to equation (2) not the thermodynamic potential itself, but an exponential function of it would be the function characteristic of the reaction. Cf. also Chem. Weekblad 7, p. 920 (1910).

$$-\frac{dc}{dt}=C\left\{e^{\frac{\Sigma \mathbf{r}_{I}\varepsilon_{0_I}-T\mathbf{r}_{I}\eta_{0_I}+\Sigma \mathbf{r}_{I}\int c_{v_I}dT-T\Sigma \mathbf{r}_{I}\int\frac{c_{v_I}}{T}dT+F_1+RT\Sigma \mathbf{r}_{I}}{RT}}\Pi c_{I}^{\nu_I}-e^{\frac{\Sigma \mathbf{r}_{II}\varepsilon_{0_{II}}-T\Sigma \mathbf{r}_{II}\eta_{0_{II}}+\Sigma \mathbf{r}_{II}\int c_{v_{II}}dT-T\Sigma \mathbf{r}_{II}\int\frac{c_{v_{II}}}{T}dT+F_2+RT\Sigma \mathbf{r}_{II}}{RT}}\Pi c_{II}^{\nu_{II}}\right\} \quad (3)$$

in which $\Pi c_{I}^{\nu_I}$ and $\Pi c_{II}^{\nu_{II}}$ represent the product of the concentrations of the first, resp. the second member of the equation of reaction, taking the number of molecules into account. If we call:

$$Ce^{\frac{\Sigma \mathbf{r}_{I}\varepsilon_{0_I}-T\Sigma \mathbf{r}_{I}\eta_{0_I}+\Sigma \mathbf{r}_{I}\int c_{v_I}dT-T\Sigma \mathbf{r}_{I}\int\frac{c_{v_I}}{T}dT+F_1+RT\Sigma \mathbf{r}_{I}}{RT}}=k_1.$$

and

$$Ce^{\frac{\Sigma \mathbf{r}_{II}\varepsilon_{0_{II}}-T\Sigma \mathbf{r}_{II}\eta_{0_{II}}+\Sigma \mathbf{r}_{II}\int c_{v_{II}}dT-T\Sigma \mathbf{r}_{II}\int\frac{c_{v_{II}}}{T}dT+F_2+RT\Sigma \mathbf{r}_{II}}{RT}}=k_2$$

(3) reduces to:

$$-\frac{dc}{dt}=k_1\,\Pi c_{I}^{\nu_I}-k_2\,\Pi c_{II}^{\nu_{II}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In the second place we must prove the validity of this formula for reactions in dilute solution. For this purpose we introduce a new quantity, μ'_1, determined by the relation:

$$\mu_1=\mu'_1+RT\log n_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

So $RT\log n_1$ is that part of the thermodynamic potential that is in connection with GIBBS's paradox, and μ'_1 the remaining part. Now as is known, the differential quotient of μ'_1 with respect to the concentrations [1]) remains finite, whereas that of the second part

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[1]) In contradiction to what is usual in the treatment of velocities of reaction, we define the concentrations here as molecular percentages of a certain substance in a definite mixture, and not as this quantity divided by the total volume. But it is clear that this does not affect the conclusions about the constancy of k_1 and k_2, as in every reaction in a dilute solution the change of volume during this reaction is disregarded.

becomes infinite for exceedingly dilute solutions. For the (of course also very slight) changes to which the concentrations in an exceedingly dilute solution can be subjected we may, therefore, consider μ'_1, μ'_2 etc. as invariable, independent of the concentrations, when we take the variations of $RT \log n_1$ etc. with the concentration into account. If we now substitute the value (5) for μ_1, and bring down the term $RT \log n_1$ from the exponent, we get again:

$$-\frac{dc}{dt} = k_1 \boldsymbol{H} n_1 - k_2 \boldsymbol{H} n'_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

where:

$$k_1 = e^{\frac{\Sigma\mu'_1 + F_1}{RT}} \quad \text{en} \quad k_2 = e^{\frac{\Sigma\mu'_2 + F_2}{RT}} \quad . \quad . \quad . \quad . \quad (6)$$

may be considered as constants according to the above, as is required by the law of the mass-action.

We conclude from this equation (4 and $4a$) that really equation (2) can properly account for a highly important property of the course of the reaction. This result was by no means to be considered as certain beforehand. For we have drawn up this equation by analogy, and drawn attention to the close agreement with the use of equation (1) in this and the preceding communication, but not to the existing differences. It is here the place to set forth these differences. It is true that in the case of the "osmotic temperatures" the final state is no state of equilibrium, but each of the two homogeneous phases may yet be considered as in equilibrium, if we leave the immediate neighbourhood of the membrane out of consideration. So we are undoubtedly justified in speaking of quantities as temperature, entropy, thermodynamic potential in each of the phases, and there the formula was applied only to that final state "of equilibrium of mass exchange". But not without justification it might be doubted whether the same thing is allowed for states in which the equilibrium of mass exchange has not yet set in, and a fortiori this holds for the case under consideration. For the homogeneous phase in which the reaction takes place, is not in equilibrium in itself; it is not certain that MAXWELL's distribution of velocities holds there, and even if with BOLTZMANN we want to introduce a definition for the entropy of a state of non-equilibrium, it will, of course, in general have another value than the η from equation (2).

Now it appears from equation (4) that all the same these undoubtedly weighty objections need not lead to a rejection of equation (2). For the very extensive material of facts concerning the reaction velocities proves conclusively that equation (4) applies to a great number of reactions that proceed with measurable velocities. Particularly it has been ascertained by numerous measurements that k_1 and k_2 are really constants in reactions that proceed normally [1]), so they are not quantities that depend on the time. If the influences which we mentioned, made themselves so strongly felt that equation (2) had to be rejected, this result would be impossible. For as the mixture more and more approaches the state of equilibrium during the reaction, and at last reaches it, the difference between the entropy which really exists at any moment (BOLTZMANN's H-function) and the entropy of the state of equilibrium will continually decrease, and at last become zero; and this remark applies to all the other mean values occurring in equation (2). But then also the k_1 and k_2 would necessarily become dependent on the time, and not only the $\Pi c_{I}^{\nu_{I}}$ and $\Pi c_{II}^{\nu_{II}}$, as experiment teaches. So we must conclude that the systems with measurable velocities of reaction may be considered as quasi-stationary systems, for which not only an entropy, a thermodynamic potential etc. exist, but for which these quantities (leaving the influence of the concentration unconsidered, of course) even differ immeasurably little from the corresponding quantities in the state of equilibrium. Now an experimentally firm basis has been given as a support for us in our further examination and development of equation (2). More particularly it has now been proved, that F_1 and F_2 can really only depend on quantities which are constant during the reaction as we supposed in § 1. However more ensues from this supposition than has been proved yet. We come back to this in § 5.

§ 3. Our second step is now to show that equation (2) differs from the equation (11) of the preceding paper holding for "osmotic temperatures" in this that here F_1 does not comprise the pure temperature functions of the thermodynamic potential with negative sign, as it did there. For the equation of the equilibrium requires the equality of the sums of the thermodynamic potentials of the two systems, and so for rarefied gases:

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[1]) We mean here by "abnormal" reactions of course reactions for which further investigation makes it plausible that the inconstancy of k is to be ascribed to after reactions, by-reactions, catalysis or too great concentrations.

$$\Sigma \mathbf{r}_{\mathrm{I}} \varepsilon_{0_{\mathrm{I}}} - T \Sigma \mathbf{r}_{\mathrm{I}} \eta_{0_{\mathrm{I}}} + \Sigma \mathbf{r}_{\mathrm{I}} \int c_{v_{\mathrm{I}}} dT - T \Sigma \mathbf{r}_{\mathrm{I}} \int \frac{c_{v_{\mathrm{I}}}}{T} dT + RT \Sigma \mathbf{r}_{\mathrm{I}} \ln c_{\mathrm{I}} + RT \Sigma \mathbf{r}_{\mathrm{I}} =$$

$$= \Sigma \mathbf{r}_{\mathrm{II}} \varepsilon_{0_{\mathrm{II}}} - T \Sigma \mathbf{r}_{\mathrm{II}} \eta_{0_{\mathrm{II}}} + \Sigma \mathbf{r}_{\mathrm{II}} \int c_{v_{\mathrm{II}}} dT - T \Sigma \mathbf{r}_{\mathrm{II}} \int \frac{c_{v_{\mathrm{II}}}}{T} dT + RT \Sigma \mathbf{r}_{\mathrm{II}} \ln c_{\mathrm{II}} +$$

$$+ RT\, \Sigma \mathbf{r}_{\mathrm{II}} \quad . \; . \; . \; . \; . \; . \; . \quad (7)$$

on the other hand equation (2) requires that:

$$\mu_{\mathrm{I}} + F_1 = \mu_{\mathrm{II}} + F_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

for the equilibrium, where the velocity $= 0$.

If F_1 were the same function as in equation (11) of the preceding paper, this would lead to:

$$\Sigma \mathbf{r}_{\mathrm{I}} \varepsilon_{0\mathrm{I}} + RT \Sigma \mathbf{r}_{\mathrm{I}} + RT \Sigma \mathbf{r}_{\mathrm{I}} \ln c_{\mathrm{I}} = \Sigma \mathbf{r}_{\mathrm{II}} \varepsilon_{0\mathrm{II}} + RT \Sigma \mathbf{r}_{\mathrm{II}} + RT \Sigma \mathbf{r}_{\mathrm{II}} \ln c_{\mathrm{II}} \quad (9)$$

and this equation is in conflict with the undoubtedly valid equation (7) as in general the specific heats of the reaction products and of the reacting substances are not equal and the constants of entropy do not occur in the latter equation. This observation is not new. It is namely at bottom identical with the argumentation on p. 45—51 in Mr. DE LANGEN's Thesis for the doctorate [1]), that the omission of the pure functions of the temperature from the formula for the thermodynamic potential for chemical reactions brings us in collision with VAN 'T HOFF's equation. For the latter is immediately obtained by differentiation from (7), whereas differentiation from (9) yields the equation of p. 46 of Mr. DE LANGEN's Thesis for the doctorate, which is in opposition to it. Mr. DE LANGEN concludes from this that the kinetic gas theory and thermodynamics are here in conflict.

But this conclusion cannot be maintained. For it has been overlooked that for the kinetic derivation of the thermodynamic potential of a mixture of chemically interacting substances, we shall have to take BOLTZMANN's [2]) "kritische Räume" into consideration, and that when the heat of reaction varies with the temperature, terms must appear which are dependent on the difference of the specific heats[3]). *What* the relation must be between these terms and the temperature and the specific heats, could only be revealed by a perfectly developed kinetic theory, which could at the same time give an account of the value of the specific heat of the different substances. So at present thermodynamics leads us further in this respect, though it naturally

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[1]) Groningen 1907.

[2]) Gastheorie II Abschnitt VI.

[3]) loc. cit. p. 199.

must leave the question undecided why and how the specific heat varies with the temperature and with the character of the substances.

§ 4. If we now compare equation (7) and (8), it appears that:

$$F_1 = F_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and as according to § 2 neither F_1 nor F_2 can be dependent on the time during the reaction, equation (8) is satisfied throughout the reaction. The same reasoning holds of course with very little change for dilute solutions too, and then also leads to equation (10). So it appears that in § 1 we have defined these functions not closely enough, when we introduced them as functions of the temperature and of constants characteristic of the reacting substances, and eventually of the occurring intermediate states. For the supposition:

$$F_1 = F_1\,(T, a_1, b_1, c_1 \ldots)$$
$$F_2 = F_2\,(T, a_2, b_2, c_2 \ldots)$$

would be in accordance with this definition, in which a_1, b_1, c_1 are characteristic of the system before the reaction, a_2, b_2, c_2 for the system after the reaction, and mutually independent. Nay, this supposition would even be the most obvious one. Equation (10), however, shows that it must be rejected. The constants in F_1 cannot be independent of those in F_2: they must be quantities which in some way or other are equally in relation with the two systems, that before and that after the reaction [1].

The simplest supposition then would be that all these constants were $= 0$, and so that F would be a pure general function of the temperature, like the $\frac{1}{2} RT \ln T$ [2] from equation (11) of the preceding paper, or that possibly this too would be wanting, and $F = 0$ might be put. However, on this supposition we come to just such an absurdity as made us reject equation (4) in the preceding paper. For from experimental determinations of:

$$k_1 = Ce^{\dfrac{\Sigma \mathbf{r}_{\mathrm{I}} \varepsilon_{0_{\mathrm{I}}} - T\Sigma \mathbf{r}_{\mathrm{I}} \eta_{0_{\mathrm{I}}} + \Sigma \mathbf{r}_{\mathrm{I}} \int c_{p_{\mathrm{I}}}\, dT - T\Sigma \mathbf{r}_{\mathrm{I}} \int \frac{c_{p_{\mathrm{I}}}}{T}\, dT + RT\Sigma \mathbf{r}_{\mathrm{I}}}{RT}}$$

and

$$k_2 = Ce^{\dfrac{\Sigma \mathbf{r}_{\mathrm{II}} \varepsilon_{0_{\mathrm{II}}} - T\Sigma \mathbf{r}_{\mathrm{II}} \eta_{0_{\mathrm{II}}} + \Sigma \mathbf{r}_{\mathrm{II}} \int c_{p_{\mathrm{II}}}\, dT - T\Sigma \mathbf{r}_{\mathrm{II}} \int \frac{c_{p_{\mathrm{II}}}}{T}\, dT + RT\Sigma_{\mathrm{II}}}{RT}}$$

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[1] So the above considerations lead to the assumption of two opposed reactions, which are, however, not 'independent' of each other. For the functions F occurs in both velocities, i.e. both partial velocities depend on the same "intermediate states".

[2] If the $\sqrt{T}$ is brought into the exponent.

at two temperatures (or the corresponding expressions for dilute solutions) we could determine $\varepsilon_{0_{I}}$, $\varepsilon_{0_{II}}$, $\eta_{0_{I}}$, and $\eta_{0_{II}}$, in other words we could find the absolute values of the energy and of the entropy experimentally, though both contain indefinite additive constants according to our definition, so that only differences of energy and entropy are liable to be measured.

So we are certain that F must contain values of energy and entropy which reduce the values of the energy and the entropy in the exponent to differences of energy and entropy. And, to confine ourselves for the present to the difference of energy, one difference of energy must determine one velocity of reaction, the other the other, their algebraic sum being the total difference of energy in the conversion, so the heat of reaction. Accordingly it is not possible that the *total* heat of reaction appears in *both* the velocities of reaction, as we might be inclined to suppose Or in other words the total heat of reaction must be split up into two parts, of which the first determines one velocity, the second the other velocity. What is now the "intermediate state", which determines this splitting up of the heat of reaction? First of all we might think of the state in which the reacting compounds are entirely split up into their atoms, so that one velocity is determined by the energy of dissociation of the reacting substances, the other by that of the reaction products. But this supposition has sense only when we assume that the reaction really takes place over the free atoms. How in the opposite case the really occurring process would be entirely determined by the then altogether fictitious heat of dissociation in the atoms, is difficult to see [1]. And though for the kinetic theory the supposition of dissociation may have some attraction, because it is an analogue to the thesis that every substance has a vapour-pressure however slight, and admits of continuous transitions, it is easy to see that the assumption of such a course "over the atoms" does not decide the question, but on the contrary only displaces and complicates the difficulty.

For when the reaction takes place over intermediate bodies present in an appreciable quantity, whatever they be, the total reaction will no longer consist of two, but of four partial reactions, because also these intermediately formed bodies will be converted to the original and the forming substances with definite velocities. The process of the reaction then becomes more complicated, and can be expressed

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[1] In our opinion quite arbitrarily TRAUTZ introduces as determinative for reactions without intermediate products the heat of splitting up of the reacting substances into atoms deprived of their kinetic energy, and a part of their potential energy (absolute zero, solid state). See TRAUTZ, Zeitschr. phys. Chem. **64** et seq.

by the following equations:

$$\frac{-dc_{\mathrm{I}}}{dt} = k_1 Hc_{\mathrm{I}} - k_{a_1} Hc_a$$

and

$$\frac{dc_{\mathrm{II}}}{dt} = k_{a_2} Hc_a - k_2 Hc_{\mathrm{II}}$$

in which the change in concentration of the intermediate product is indicated by:

$$\frac{dc_a}{dt} = -\frac{dc_{\mathrm{I}}}{dt} - \frac{dc_{\mathrm{II}}}{dt} = k_1 Hc_{\mathrm{I}} - k_{a_1} Hc_a - k_{a_2} Hc_a + k_2 Hc_{\mathrm{II}} .$$

So in general the velocity will not be represented by the simple expression of the law of mass-action [1]); this is the case only when k_{a_1} and k_{a_2} are both very great with respect to k_1 and k_2, in other words when no appreciable quantities of the intermediate products occur in the reaction mixture [2]).

An example of this furnishes the reaction $Ni + 4CO \rightleftarrows Ni(CO)_4$, in which the measurements of the velocity show that the reaction takes place from the left to the right over $Ni(CO)_2$, which, however is so quickly decomposed, and combines so rapidly with an excess of CO (k_{a_1} and k_{a_2} great), that it cannot be demonstrated in the reaction mixture.

But there is little reason to assume that every reaction should be thought to be such that the reacting substances break up into pieces (either atoms or groups of atoms), which unite again as free components in another way; on the contrary room should be left for the possibility that throughout the reaction no other independently moving particles occur than the molecules of the initial and the final products. This supposition is undoubtedly greatly supported by the fact that substances which are in themselves exceedingly stable, and do not present the slightest trace of dissociation in pure condition at a definite temperature, are yet liable to be analysed by means of an added substance. If to take a concrete example, we consider the reaction:

$$H_2 + Cl_2 \rightleftarrows 2HCl$$

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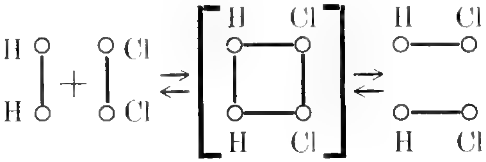
[1]) That in this case the reaction heat must be split up into two parts one of which is the heat of reaction of the decomposing substances in the intermediate product, the other that of the forming substances into the intermediate body, seems to us not doubtful; this refers, however, to the splitting up of a constant of equilibrium into two other constants of equilibrium, each of which must then again be split up into two constants of velocity.

[2]) Zie SCHREINEMAKERS Chem. Weekblad I. 625 (1904).

at least the possibility will not be denied that the reaction does not take place so, that H_2 and Cl_2 are dissociated to atoms H and Cl, and these atoms meet again with formation of HCl, but so that a molecule H_2 meets a molecule Cl_2, and that with a suitable position of these molecules the bond between the H atoms and the Cl atoms inter se is only broken in consequence of the mutual attraction of the H and the Cl atoms and immediately passes into a new bond. If we imagine the course of the reaction in this way, a value of the energy may be indicated which undoubtedly with greater justice may be expected to determine the velocity of reaction than the heat of dissociation in the atoms which is here devoid of any chemical significance. In consequence of the approach of the molecules H_2 and Cl_2 there is, namely, a certain loss of potential energy through the action of the attracting forces; when the two molecules have approached each other to a certain distance, the potential energy will attain a minimum value, a condition which is indicated by what is contained between the brackets in the following symbolic representation:



If then the molecules of hydrochloric acid again separate, the potential energy will rise again in consequence of the work done against the attractive forces.

Now in our opinion it may certainly not be considered as impossible that this state of minimum potential energy is to be considered as the above-mentioned "intermediate state". In the value of F of equation (10) the corresponding potential energy and entropy, at least the corresponding constants, will have to occur.

We may state once more that we by no means mean to say that in the mentioned reaction, or any other reaction, the process must be exactly as we sketched it. We only wanted to make clear first of all that it necessarily follows from the value for k that "intermediate states" play a part; further that these intermediate states may be of various kinds, and can be entirely different in one reaction from that in another. So a *universally* holding splitting up of the heat of reaction into two parts, for reactions in which no intermediate products occur, as of late was tried by TRAUTZ, will probably be impossible. There is still less chance that it is to be decided now, whether besides the quantities determined by the "intermediate state" there is still a general function of the temperature, as $1/2 RT \ln T$ which occurs in F.1) Only a further development of the kinetic theory and an accurate analysis of the experimental material in the light of such a theory, can lead us further.

§ 5. We must now return to the conclusion of § 2. We said there that there is more involved in our suppositions about F_1 and F_2 than could be proved by the facts mentioned there. For these prove that F can only depend on quantities constant in the reaction. If we now imagine a reaction in rarefied gas state, in which the total number of molecules changes, then the concentrations, the pressure, and the specific volume change during the reaction. So in this case these quantities cannot occur in F. But by far the most important part of the material concerning the law of the mass-action refers to reactions in dilute solutions, and during these reactions the pressure does not change. If we want to compare our supposition that F does not depend on the pressure with the experiment for these reactions, we must examine the influence of the pressure on the velocity of reaction. In this we must, however, take note of a circumstance, which it was unnecessary to mention expressly in the foregoing discussion: the influence of catalytic agents 2), and that because in general the possibility exists that the solvent itself works as a catalytic agent, i.e. that the solvent participates in the "favourable" collisions, and thus occasions the exchange of the absorbed resp. generated heat. So we shall have to keep the possibility in view that the presence of the solvent, or of other dissolved substances, whose quantity remains invariable catalytic agents) is yet of great influence on the velocity of reaction. According as this influence in this sense exists or does not exist, the thermodynamic potential of these substances must be added to the other thermodynamic potentials in equation (6).

Let us now first consider the case that neither the solvent nor the catalytic agent takes part in the collisions favourable for the reaction, we shall have to sum the μ'_1 of the different reacting substances

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1) See TRAUTZ papers Zschr. f. phys. Ch. 64, et seq. and SACKUR's criticism of them Zeitsch. f. Elektroch. **15** (1909).

2) We refer to homogeneous catalysis, as appears from the text. Also elsewhere in this paper we have disregarded heterogeneous catalysis, particularly in the gas-reactions discussed in § 2, which we assumed to take place in the homogeneous phase, leaving undecided whether such reactions really occur, or whether every gas-reaction represents a case of heterogeneous catalysis.

under the Σ sign in equation (6), whereas F is only dependent on the temperature and on the quantities characteristic of the different substances according to our suppositions. Hence

$$\frac{dlk}{dp} = \frac{1}{RT} \frac{\Sigma d\mu'_1}{dp}$$

or as according to equation (5)

$$\frac{\partial \mu'_1}{\partial p} = \frac{\partial \mu}{\partial p}$$

$$\frac{\partial lk}{\partial p} = \frac{1}{RT} \left(\frac{\partial \Sigma \mu_1}{\partial p} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Now for a mixture of n components, of which resp. $n_1 . n_2 \ldots n_n$ gram-molecules are present

$$d\varepsilon = Td\eta - pdv + \mu_1 dn_1 + \mu_1 dn_2 \ldots \mu_n dn_n$$

where μ is the molecular thermodynamic potential.

Or:

$$d\zeta := - \eta dT + vdp + \mu_1 \, dn_1 + \mu_2 \, dn_2 \ldots \mu_n \, dn_n$$

and so:

$$\left(\frac{\partial \mu_1}{\partial p} \right)_{T,n_1,n_2 \ldots n_n} = \left(\frac{\partial v}{\partial n_1} \right)_{p,T,n_2 \ldots n_n}$$

in consequence of which (11) passes into:

$$RT \frac{dlk}{dp} = \Sigma \left(\frac{\partial v}{\partial n_l} \right)_{p,T,n_1,n_2 \ldots n_k,n_m \ldots n_n} = \left(\frac{\partial v}{\partial n_1} \right)_{p,T,n_2 \ldots n_n} + \left(\frac{\partial v}{\partial n_2} \right)_{p,T,n_1 n_3 \ldots n_n} + \text{etc.} \quad (12)$$

So in order to examine the change of the velocity of reaction with the pressure, we have to determine for every substance of the disappearing system (resp. the forming system) the change of volume, which takes place when we add one gram molecule to the whole system (reacting substances, reaction products, solvent), the quantity of this last being thought so great that it does not change the concentrations. The sum of these variations gives $\frac{dlk}{dp}$.

It is clear that it will be a great exception if one of the quantities $\left(\frac{\partial v}{\partial n} \right)$ becomes negative. For this would mean that there was a contraction so considerable that the mixture occupies a smaller volume after the mixing than the solvent alone. Yet it must not be considered as impossible a priori, and a negative value of $\left(\frac{\partial v}{\partial n} \right)$ seems even to occur for some aqueous solutions. It is, however, required for a negative value of $\frac{dlk}{dp}$, that the sum of $\left(\frac{\partial v}{\partial n}\right)$ becomes negative for all the substances of the system, and this is of course, still less probable. Hence it may be safely assumed that a negative value of $\frac{dlk}{dp}$ will not occur in the case considered up to now. When the solvent takes part in the reaction (in the above-mentioned sense, that only those collisions are favourable in which also the solvent participates, so without change of its quantity during the reaction), also the thermodynamic potential of the solvent will have to be inserted under the Σ sign in our equation. So in equation (12) one more term $\left(\frac{\partial v}{\partial n}\right)$ will occur on the right side, which refers to the solvent. This will, however, not easily affect our conclusions about the sign of $\frac{dlk}{dp}$. It is, however, a different matter, when also a catalytic agent plays a part. If e.g. we think the H-ions of an added acid active as a catalyser, the change of the thermodynamic potential of these H-ions with change of the pressure will not be represented by a term as $\left(\frac{\partial v}{\partial n}\right)$, because there neither the possible modification of the degree of dissociation by the increase of pressure, nor the appearance of hydrate-ions has been taken into account. So the fact that ROTHMUND found a negative value of $\frac{dlk}{dp}$ in the conversion of cane-sugar under influence of HCl, need not be in contradiction with equation (2), and equation (12) derived from it. In the few other cases known to us, where the influence of the pressure on the velocity of a reaction has been examined, a positive value is found, but this experimental material is certainly still too scanty to justify a conclusion concerning equation (2). A more complete knowledge of the facts, preferably concerning reactions where the last mentioned complications do not occur, might possibly enable us to decide about the suppositions which lead to equation (2).

Other conclusions from equation (2), which may be tested by experiment, will be found for concentrated solutions. For it is clear, that then the values μ'_1 etc. must no longer be considered independent of the concentrations, in other words that the k_1 and k_2 can no longer be constant, so that deviations from the law of mass-action present themselves, as has actually been found in the inversion of cane-sugar. We hope to return to this point later on.

§ 6. Here we intend only to add some general remarks in connection with the above-given considerations. For even though we emphatically point out that we are entirely in the region of suppositions about the nature of the "intermediate states" holding for every reaction, we consider it proved by the considerations of § 4 that for every reaction[1] such "intermediate states" must possess a real signification as far as their velocity is concerned. And in consequence of this we think we are able, also in connection with the other considerations which we have given in this communication, to make an attempt to give a more general and lucid classification of the conception catalysis and allied phenomena, than had been possible up to now. In doing this we shall have to distinguish strictly — as Van 't Hoff already does in his Vorlesungen Heft I p. 210 et. seq. — between influences which only affect the velocity, the real catalytic agents and "shifters of the equilibrium". Hence we distinguish the following cases:

1. A reaction which does not take place between the pure substances, or which only proceeds slowly, is started or accelerated by a substance which is present in small quantity and does not take part in the reaction. The equilibrium that establishes itself is, however, independent of the nature of the catalytic agent. We think e.g. of the equilibrium acetaldehyde, paraldehyde, metaldehyde or of the conversion of oxyhydrogen gas. For each of these cases we have undoubtedly to do with phenomena of retardation, false equillibria; the condition without a catalytic agent is, indeed, a local maximum of entropy at given energy, but not an absolute maximum. The catalytic agent does not change the specific energy or entropy of the substances in any respect, but only enables them to reach the absolute maximum of entropy by change of concentration. So it may be compared to a crystal brought into a supercooled liquid. But what was said in § 4 can make this action somewhat clearer to us. This action consists in the creation of an intermediate state, or if this existed already in changing its potential energy in consequence of which the difference of energy which determines the velocity, is increased. Different catalytic agents act differently in this respect, and so they give rise to another velocity.

2. A substance which is added in an exceedingly slight quantity not only changes the velocity of reaction, but also the equilibrium.

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[1] Perhaps pure dissociations e.g. $N_2O_4 \rightleftarrows 2NO_2$ will only have to be excepted.

Such an influence[1]) would occur, if the specific entropy of the parts of the reacting mixture should be changed by the catalytic agent, but not the specific energy. The mutual entropy of the system catalytic agent + reacting mixture in the ideal gas state would have another value in this case, than is given by GIBBS's paradox, while as usually in the ideal gas state no mutual energy would occur. To explain this we should have to accept a change of the chemical volumes (BOLTZMANN's "kritische Räume") of the reacting mixture by the catalytic agent. A modified intermediate state would, of course, occur here too; hence the equilibrium will be reached with another velocity.

3. By the addition of a substance which does not take part in the reaction also the specific energy of the reacting substances is changed either because only the mutual attraction in the mixture becomes different — new *a*'s appear in the equation of state — or because stronger causes are active (association of the solvent with one of the reacting substances). Of course also the velocity of reaction will change in both cases. To this category belong all "milieu" influences, of course, (e. g. changes of electrolytic dissociation with change of solvent). Also the displacements of the equilibrium under influence of light or electric discharges may belong to it, e. g. the light-equilibrium of sulphur in CS_2, which sets in with a certain intensity of illumination, and which returns to its former state when the old state of illumination is restored. Here too it must be assumed that in consequence of the illumination the energy of the reacting substances is modified[2]).

4. The last mentioned cases, however, can also belong, either all of them or partly, to another category. For it is possible that they are no real equilibria, but are in the same relation to them as the case of the "osmotic temperatures" to that of real equilibrium, or in other words that the modified state must always be accompanied by a "current of energy", an absorption of heat or electric energy and emission of heat. Then the displacement would not be maintained

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[1]) We will leave it an open question whether the cases cited as such in the literature should not really be ranged under 3, but think that we should at least mention this possibility for completeness' sake because the considerations of VAN 'T HOFF l.c. p. 21 which indeed only seem to be intended for heterogeneous catalysis, do not prove as far as we can see, that a case of homogeneous catalysis of this kind is excluded by the second law of thermodynamics.

[2]) Cf. SMITS. These Proc. XII p. 356. Of course the false equilibria, which are reduced to the absolutely stable state by light or an electric spark do not belong to this category; they belong under 1.

if we could enclose the system between absolutely reflecting walls in the new state, and if we could thus maintain the same state of radiation, but without absorption of new energy. Such a system would no longer respond to the laws of thermodynamics, even if we included among them the thermodynamics of radiation, in the same way as we found that for the "osmotic temperature" the thermodynamic law of constancy of the thermodynamic potential is not fulfilled. Our experimental and theoretical knowledge is not sufficiently advanced to decide whether the photo- and electrochemical "equilibria" belong to this or the preceding category [1]).

Physics. — "*Some remarks on the mechanical foundation of thermodynamics.*" I. By Dr. L. S. Ornstein. (Communicated by Prof. H. A. Lorentz).

(Communicated in the meeting of December 24, 1910).

In order to deduce the second law of thermodynamics the theory of ensembles of systems is often used. This theory has been largely discussed by J. W. Gibbs in his well-known Elementary Principles of Statistical Mechanics. In his book two kinds of ensembles, the canonical and the microcanonical, come to the fore. The latter kind of ensembles has been used by Dr. Paul Hertz who held some views which give me occasion for a few remarks [2]).

§ 1. In the beginning of his paper Dr. Hertz explains that it is rational to use for the study of the phenomena shown in a given system the ensemble of states taken by that system when left to itself. Such an ensemble is usually termed a time-ensemble. As the observed phenomena must be considered as the result of many phases adopted by the system during the time of observation, we have every reason to presume, that our observation teaches us something of the mean value in the time-ensemble. By using the terminology of poly-dimensional geometry we can put the following

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[1]) We will point out that it is sometimes still impossible to assign a place in this classification to a phenomenon in the department of catalysis. It is e. g. difficult to explain in what connection with the mentioned cases the fact is that the thermodynamic potential of perfectly dry solid NH_4Cl is so considerably modified by the addition of the slightest trace of moisture, as appears from the totally modified partial vapour pressure of the NH_4Cl molecules. Perhaps this case will appear to be an example of 2.

[2]) Ann. der Phys. Bd. **30**, p. 236, 1910.

considerations in a geometrical form. The state of a given system of n degrees of freedom is determined by n general coordinates $q_1 \ldots q_\nu \ldots q_n$ and the n corresponding momenta $p_1 \ldots p_\nu \ldots p_n$. If we take these $2n$ variables as the coordinates of a point in a space R_{2n} (extension in phase) a point of this space will then represent the state of a system.

All the points taken by the representing point for a system left to itself, will lie in a $(2n-1)$-dimensional space E_{2n-1}, of which the equation is as follows:

$$\varepsilon\,(p_1 \ldots p_\nu \ldots p_n,\ q_1 \ldots q_\nu \ldots q_n) = C \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The form of the function ε, which represents the energy, depends on the kind of the given system. The motion of the representing point in the space E_{2n-1} is determined by $2n$ differential equations of the form

$$\dot{p}_\nu = -\frac{\partial \varepsilon}{\partial q_\nu}$$

(ν taken from $1-n$)

$$\dot{q}_\nu = \frac{\partial \varepsilon}{\partial p_\nu},$$

and by the $2n$ initial values of the p's and the q's. The point passes through a line in the space E_{2n-1}, which I shall indicate as the trajectory L. Like EINSTEIN [1]) Dr. HERTZ assumes that the trajectory L perfectly fills the whole space E_{2n-1}. Making use of this hypothesis they then demonstrate that the mean value of a quantity in a time-ensemble is identical with that in the microcanonical ensemble. For this reason, it is possible, to reduce the study of the properties of an arbitrary system to that of a microcanonical ensemble. This ensemble consists of a layer between the spaces ε and $\varepsilon + d\varepsilon$ filled homogeneously with systems of a ϱ_{2n} density. If in the limit $d\varepsilon$ is taken equal to 0 and ϱ_{2n} to infinite, but in such a way that $\varrho_{2n}\, d\varepsilon$ remains finite, we get an ensemble in the space E_{2n-1} which is filled with a space density ϱ_{2n-1}; the thus formed ensemble will be called an energy-space ensemble. We have to specify the terms mean value in an ensemble and probability of a state. Before I pass on to that, I shall examine more closely the hypothesis already mentioned of EINSTEIN and HERTZ.

It is impossible for a system to pass rigidly in a finite time (whatever length it may have) through all the possible phases; and in calculating a time-average such a finite time must be imagined.

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[1]) A. EINSTEIN, Ann. d. Phys. Bd. 11, p. 170, 1903.

Poincaré and Zermelo have elucidated that the trajectories of the systems are in general closed and there are many cases in which we find closed trajectories which do certainly not pass through all the points of the space E_{2n-1}. I shall give some examples as an illustration of this. If the kinetic energy which we have adopted using the dynamical equations in the canonical form, is a homogeneous quadratic function of the momenta (the coefficients being functions of the coordinates), the system in which the momenta have been reversed, will be represented in the same space E_{2n-1}. A certain path L being given, we can attain another possible path L' by reversing the momenta at all points a, b, c of the path L; and the path L' can be passed through in such a way that the interval of time between the two moments at which the positions b' and a' are reached is equal to that between the moments at which first a and b were attained. I shall term those systems reversed systems, their paths reversed paths. It is now not necessary that the path and the reversed path are parts of the same trajectory and if they are not, there exist at least two totally insulated trajectories in the space E_{2n-1} and each of them cannot possibly run through all the points of E_{2n-1}. In order to give a simple example, we might consider the following case; within a sphere two material points are moving with equal velocity, which are reflected mutually and through the walls as perfectly elastic bodies. We can choose of all possible motions that one in which the two points move along the sides of a square. Now two assumptions are possible:

1. The points move in the same direction; in that case the reversed path will never be reached.

2. The points move in opposite direction; the path and the reversed path will be the same.

Placing more points into the sphere we can, even if we ascribe a finite extension to the points, so that the distribution of velocities may be changed by the mutual impacts, always find an initial state such that in one case the path and the reversed are the same and in the other case not, while all the trajectories lie in the same space E_{2n-1}[1].

One might ask if in case the path of a system does not exactly reach each point of the space E_{2n-1}, it could not be possible that in the course of a sufficiently long time it would pass as near each point as we want to? In simple systems having a certain regularity this is impossible; what will be the case with complicated systems

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[1] Compare Kelvin Baltimore lectures p. 486.

with a great number of degrees of freedom, it is very difficult to say in general. It appears to me that it will be very rare in any case for a system which is in a "molekular ungeordnet" state to pass to a "molekular geordnet" one.

Meanwhile a circumstance appears which is favourable for the hypothesis of HERTZ and EINSTEIN. Though many phases may exist that cannot be attained by a determined path, these phases can be indiscernible for observation, for we shall find the same observed data for systems widely differing in internal state. Taking together all these "equivalent" states and paths, we get an important extension of the ensemble which can be used to deduce something about the observed quantities. And though there is, strictly speaking, no direct connection between the systems taken into account, our results may teach us something of the systems of observation.

Another favourable circumstance is that a great part of the systems of a microcanonical ensemble differ very little. The same is true for the states which a system successively passes through. The system, equivalent to the greater majority of the states consecutively passed through, may be the same as that which is equivalent to the majority of the systems of a microcanonical ensemble. (The same is true for a canonical ensemble).

Prudence is however recommended not to generalise this result. Take for example the case of a large number of perfectly smooth and rigid spherical molecules enclosed in a spherical vessel, which walls are supposed perfectly elastic and smooth with respect to the molecules. The resulting moment of momenta with respect to the centre is now constant. If an initial state has been given the coordinates of the representing point are limited by the equations

$$\left.\begin{array}{r}\varepsilon = C \\ M = M_0\end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

M is a known function of the coordinates and the momenta. The path of the system will now be confined, to the $2(n-1)$-dimensional space (2), points of E_{2n-1} lying outside (2) are never reached. For the majority of the systems possessing a given energy however the moment M will differ only little from 0. If one divides the space E_{2n-1} by spaces $M = 0$, $M = \delta \ldots$ in layers, then the majority of the systems will be situated in the layer ($M = 0 \ldots M = \delta$), where δ is a very little quantity. The systems of each layer will be equivalent for the greater part. Though the path of the representing point may not pass through all the points, we shall find results of very fair approximation if we take into account the whole space E_{2n-1}. [1])

§ 2. Before applying the theory of the ensembles to the consideration of real systems, I shall point out somewhat more accurately the idea of mean value and probability. Let us suppose φ to be some quantity relating to a given system, the value will be a function of the time. The mean value of φ in a time-ensemble between the time t_1 and t_2 shall be given by the formula:

$$\overline{\varphi}\Big|_t = \frac{1}{t_2-t_1}\int_{t_1}^{t_2} \varphi\, dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

If we determine the value of a quantity φ (for example a pressure, temperature, or density) it is not the value for a given moment that comes to expression in our measurements, but a quantity depending on the values taken by it in the course of the time. It is obvious to suppose that the mean value as it has been given by (3), is the quantity found by our observations [2]).

Making use of this hypothesis we may ask for which of the time-ensembles imaginable in the space E_{2n-1} we have to apply

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[1]) The fact that in the case mentioned above the quantity M for the greater part of the systems of a microcanonical ensemble is 0, shows that we cannot use these ensembles for those cases in which the moment deviates from 0. We can use for those cases an ensemble formed in the space (2), but it will be more convenient to use an extension of the canonical ensembles which has been indicated by Gibbs (p. 38). In this kind of ensembles the number of systems lying in an element $dp_1 \,.\,.\, dq_n$ of R_{2n} can be represented by

$$N e^{A - \frac{\varepsilon}{\Theta} - \frac{M}{M_0}} dp_1 \ldots dq_n,$$

the quantities Θ, M_0 and A are constants. Without going into details for the moment, I will only remark that in the part of the space in the neighbourhood of ($\varepsilon = \varepsilon_0$, $M = M_0$) the density surpasses that for all the other parts greatly

[2]) To prove in general that it is this quantity which determines the observed value of φ will be difficult, for the pressure the proof has been given.

In the case of a quantity changing with the time we can still use (3) to define the value for an interval of time that is sufficiently small to allow us to neglect the change of the observed quantity. The formula (3) however may be used only if $\overline{\varphi}\Big|_t$ does not depend on the length of the interval $t_2 - t_1$. It must be possible for the divergences between φ in $\overline{\varphi}\Big|_t$ to compensate each other. In the case that $\overline{\varphi}\Big|_t$ changes with the time the interval for which $\overline{\varphi}\Big|_t$ can be treated as a constant must be sufficiently long to allow the compensation of the negative and positive values of $\overline{\varphi}\Big|_t - \varphi$.

the formula (3) and for which interval in the chosen time-ensemble. Of course this question cannot be answered. We can only remark that as well for the majority of all intervals in the same time-ensemble as for the majority of all time-ensembles (3) has the same value. This value is that of q for a stationary system.

Instead of paying attention to the phases taken successively by a single system and to unite these to a time-ensemble we can imagine the path L filled with some distribution of systems. This kind of ensembles I shall call line-ensembles. The number of systems on an element ds of the path is represented by $\varrho_1\, ds$. The line-ensemble is stationary if the number of points on the line does not change by the motion of the representing points. It is easy to indicate the condition necessary for ϱ_1 in a stationary line-ensemble.

Let P and P' be two points of the trajectory L and v and v' the velocity of the representing point while ϱ_1 and ϱ'_1 represent the density in their immediate vicinity. The number of systems lying on the part PP' of L does not change by the motion of the systems if

$$v\,\varrho_1 = v'\,\varrho'_1 .$$

So the line-ensemble is stationary if ϱ_1 is represented by

$$\varrho_1 = \frac{c}{v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The mean value of a quantity q, having a definite value for each system, can be defined by

$$\overline{q}\Big]_s = \frac{\int_{s_1}^{s_2} \varrho\, q\, ds}{\int_{s_1}^{s_2} \varrho\, ds} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In this formula s_1 and s_2 denote the distance from P_1 and P_2 to a fixed points P_0 measured along the line L. For the stationary line-ensemble we find

$$\overline{q}\Big]_s = \frac{\int_{s_1}^{s_2} \frac{1}{v}\, q\, ds}{\int_{s_1}^{s_2} \frac{ds}{v}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The value of $\overline{\varphi}\Big|_s$ is equal to that of $\overline{\varphi}\Big|_t$ for the corresponding interval, as is easily seen if one thinks that $\frac{ds}{r}$ represents the time taken by the system to pass through ds. The stationary line-ensemble can therefore be used to determine the value of observed quantities.

I shall now consider another kind ef ensembles. We divide the space E_{2n-1} in elements in the following manner. Let P be a point of this space and L the trajectory through this point. Put in P a space R_{2n-1} perpendicular to L and in the section of E_{2n-1} and R_{2n-1} a $(2n-1)$-dimensional element of volume do, containing P. Through the limits of do the lines L are drawn and in a point P' on L at a distance ds from P a space R'_{2n-1} perpendicular to L is constructed. This cuts the paths drawn from do; in the space (E_{2n-1}, R'_{2n-1}) an element of volume is formed, which is equal to do (differing only from it in the order of ds).

The volume of the part of the space E_{2n-1} limited by the elements do and the lines L amounts to $ds\, do$.

We take the element do so small that r may be thought equal for all points of it and fill the element with a density $\frac{A}{r}$ with representing points. The number of systems in $do\, ds$ amounts to

$$do\, ds\, \frac{A}{r}\,,$$

or if we put $do\, ds = d\omega$

$$d\omega\, \frac{A}{r}\,.$$

The mean value in such an ensemble shall be defined by

$$\overline{\varphi}\Big|_{\xi} = \frac{\int_{\xi} \frac{\varphi}{r}\, d\omega}{\int_{\xi} \frac{d\omega}{r}} \qquad \text{. . . . . (7)}$$

the integration has to be extended over the whole space E_{2n-1}. The definition has been chosen thus because the contribution for a strip of the breadth do between P and P' (s_1 and s_2) then amounts to

$$\frac{do \int_{s_1}^{s_2} \frac{\varphi}{r}\, ds}{do \int_{s_1}^{s_2} \frac{ds}{r}}$$

which for the limit $do = 0$ is equal to $\overline{q}\,\big|_t$ [1]). I would be possible to take the constant A different for the several strips in which E_{2n-1} can be divided; the ensemble attained in this way is also stationary [2]). I shall prove that the ensemble with A constant (the energy-space ensemble) is the limit of a microcanonical ensemble. In order to prove this, it is necessary to consider more closely the velocity v. If we take a point $p_1 \ldots . q_n$ it is easy to indicate the components of v; these are:

$$\left.\begin{aligned} \dot{p}_\nu &= -\frac{\partial \varepsilon}{\partial q_\nu} \\ \dot{q}_\nu &= \frac{\partial \varepsilon}{\partial p_\nu} \end{aligned}\right\} \nu \text{ from } 1-n$$

therefore

$$v^2 = \sum_1^n \left\{ \left(\frac{\partial \varepsilon}{\partial p_\nu}\right)^2 + \left(\frac{\partial \varepsilon}{\partial q_\nu}\right)^2 \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This velocity can be connected with a purely geometrical quantity relating to the space E_{2n-1} in the point p_ν, q_ν.

The direction-coefficients of the normal on this space in the point in question (α_ν, β_ν) are:

$$\alpha_\nu = \frac{\dfrac{\partial \varepsilon}{\partial q_\nu}}{\sqrt{\sum\limits_1^n \left\{ \left(\dfrac{\partial \varepsilon}{\partial q_\nu}\right)^2 + \left(\dfrac{\partial \varepsilon}{\partial q_\nu}\right)^2 \right\}}}$$

$$\beta_\nu = \frac{\dfrac{\partial \varepsilon}{\partial p_\nu}}{\sqrt{\sum\limits_1^n \left\{ \left(\dfrac{\partial \varepsilon}{\partial q_\nu}\right)^2 + \left(\dfrac{\partial \varepsilon}{\partial p}\right)_\nu^2 \right\}}} .$$

Let $\angle$ denote a distance on the normal, ending on the space E_{2n-1}, $\varepsilon + d\varepsilon$, we shall have

$$d\varepsilon = \angle \sum_1^n \left\{ \frac{\partial \varepsilon}{\partial q_\nu} \alpha_\nu + \frac{\partial \varepsilon}{\partial p_\nu} \beta_\nu \right\} = \angle\, v$$

If $\angle$ approaches 0 we find $\dfrac{d\varepsilon}{dN}$, i.e. the differential-coefficient of ε in the direction of the normal at the space E_{2n-1}. Or therefore,

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[1]) I shall prove that do is absolutely constant for a strip.

[2]) An ensemble of this kind is produceed by cutting through the space E_{2n-1} a layer from the ensemble of page 808.

$$\frac{\partial \varepsilon}{\partial N} = v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Let us now consider a layer between the spaces E_{2n-1} for ε and E_{2n-1} for $\varepsilon + d\varepsilon$ as the values of the energy, and let us divide this layer on the following way in elements. If P is a point in the space E_{2n-1} and L the path of the system through the point, R_{2n-1} perpendicular to L, we shall take in the section of E_{2n-1} and R_{2n-1} an element do and draw the trajectories through the limits of it, let now further P' be a point on the path L and R'_{2n-1} a space perpendicular to L, in this space an element do' is formed by the trajectories. Now at the points of do and do' we construct the normals on E_{2n-1}, these lines cut E'_{2n-1}, and in this manner there are formed $(2n-1)$-dimensional space elements of the volumes $\angle do$ and $\angle' do'$; the distance of the space E_{2n-1} and E'_{2n-1} at the points P and P' respectively is designate by $\angle$ and $\angle'$. In the time dt all the systems cross the elements which are situated in the volumes $v do \Delta dt$ and $v' do' \angle' dt$. But Liouvilles' theorem teaches us that these volumes are equal, therefore:

$$do \angle v = do' \angle' v'.$$

Taking into account the relation (9) we find:

$$do \, d\varepsilon = do' \, d\varepsilon$$
$$do = do'.$$

We must now suppose that the space between E_{2n-1} and E'_{2n-1} is filled everywhere with a homogeneous density ϱ_{2n}; in this way the microcanonical ensemble of Gibbs is constituted. In an element of the layer $do \angle ds$ lie $\varrho_{2n} do \angle ds$ systems, ds is an element of length of the path L. The last expression can be transformed into

$$\varrho_{2n} \, d\varepsilon \, \frac{do \, ds}{v}.$$

If we let now $d\varepsilon$ approach to 0 and $\varrho_{2n} d\varepsilon = A$ remains a finite constant, we find in the limit a distribution in the space E_{2n-1} with the density ϱ_{2n-1}

$$\varrho_{2n-1} = \frac{A}{v}.$$

Therefore the energy space-ensemble is the limit of the microcanonical ensemble.

By the probability of a system I understand the number of systems in an element of volume that surrounds the point representing the system under discussion, divided by the total number of systems in the ensemble.

We shall represent this probability by w, suppose w_1 and w_2 to be the probabilities of two different states, then we have for the line-ensemble

$$\frac{w_1}{w_2} = \frac{v_2}{v_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10);$$

for the energy space-ensemble

$$\frac{w_1}{w_2} = \frac{r_2}{r_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11);$$

for the microcanonical and the time-ensemble

$$w_1 = w_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12).$$

We can represent the probability of a given system by

$$w = \frac{C_1}{v}$$

for the line-ensemble,

$$w = \frac{C_2}{r}$$

for the energy space-ensemble and

$$w = C_3$$

for the microcanonical ensemble [1]).

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[1]) In order to determine the constants C_2 and C_3 we can proceed in the following way. The number of systems in an element $d\omega$ of the energy space-ensemble and in an element $dp_1 \ldots dq_n$ of the microcanonical ensemble amounts to $\frac{NC_2}{r} d\omega$ and $N^1 \, C_3 \, dp_1 \ldots dq_n$, if N and N^1 represent the total number of systems in the ensemble. It is easily shown now that we have

$$C_2^{-1} = \int\limits_E \frac{d\omega}{r} = \int\limits_E \frac{d\omega}{\frac{\partial \varepsilon}{\partial N}}$$

where the integration has to be extended over the space E_{2n-1}. And further

$$C_3^{-1} = \int dp_1 \ldots dq_n =$$
$$= \int\limits_{\varepsilon} d\omega L = d\varepsilon \int\limits_E \frac{d\omega}{r},$$

the integral $\int\limits_{\varepsilon}$ has to be extended over the layer between E_{2n-1} and E'_{2n-1}, and the integral $\int\limits_E$ again over the space E_{2n-1}.

In determining the constant C_1 we have to distinguish between two cases. In the first place if the path L is closed we find

If it is natural to use the line-ensemble for the definition of the probability of a real system, we see by the preceding discussion that the energy space-ensembles are also natural for this purpose. It may be noticed that in all those ensembles the majority of the systems are equivalent for observation. If we take the probability equal for all those equivalent systems, we find a large group which have a greater probability than all the other systems of the ensemble

§ 3. Let us consider the velocity in some special cases. We have found for the velocity

$$v^2 = \sum_1^n (\dot{p}_\nu^2 + \dot{q}_\nu^2).$$

Suppose that the kinetic energy gets the form

$$\varepsilon_p = \frac{m}{2} \sum_1^n \dot{q}_\nu^2 \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

then we have

$$v^2 = \frac{2}{m} \varepsilon_p + \sum_1^n \left(\frac{\partial \varepsilon}{\partial q_\nu}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Let us begin with the case that $\frac{n}{2}$ material points are enclosed within a given volume. We assume that the points do not exercise any mutual action, that, however, the walls of the vessel repulse them with forces which become infinite when a point has penetrated a very short distance σ into the wall. Within the vessel up to the walls the forces are neglectable. The points will move into the walls until their kinetic energy has been exhausted; they then possess a finite potential energy. During a collision with the walls $\left(\frac{\partial \varepsilon}{\partial q_\nu}\right)^2$ is very great in comparison to the potential energy.

$$\int w ds = 1 = C_1 \int \frac{ds}{v} = C_1 T$$

or

$$C_1^{-1} = T$$

the integral taken thus over the path of the system, T is the time which the representing point requires to get round the trajectory.

In the second place the path can be open, the time T becomes then infinite; we have to restrict ourselves to the formula (10). If, however, the path returns to the initial phase in a time T' without exactly reaching it, it is possible that always after the period T' the same phases are approximately reached. In this case w the probability of the phase might be defined by the equation:

$$w = \frac{1}{v\,T'}$$

We put the expression for v in the form

$$v^2 = \frac{2}{m}\varepsilon - \frac{2}{m}\varepsilon_l + \sum_1^n \left(\frac{\partial\varepsilon}{\partial q_\nu}\right)^2 .$$

It is easily seen that v is constant $\left(=\sqrt{\frac{2\varepsilon}{m}}\right)$ as long as no point is in collision with the walls. During the times that there are one or more collisions with the walls, v is much larger than $\sqrt{\frac{2\varepsilon}{m}}$, as the third (positive) term surpasses the second (negative). We suppose the time of collision to be very short. The path of the representing point $\int v\,dt$ during the collision remains finite (also if d approaches 0). The path of the representing point is such that if there are no collisions the p_ν are constant, while the q_ν are changing linearly with the time, while during a collision the representing point "springs" in a very short time to a new position, where all the q_ν remain the same and also the p_ν except those which correspond to the material point, which has suffered the collision. In both cases the trajectory can never cut itself, if it returns in the same point, it must be closed.

We can distinguish two extreme cases: 1st. the collision lasts very short in comparison to the average time between two successive collisions and 2nd. the reverse is the case.

In the first case the velocity will, during intervals which are of the same order of magnitude as those between the collisions, have the value $\sqrt{\frac{2\varepsilon}{m}}$ and it will largely deviate from this value during very short intervals. If we represent v as a function of the time by a graph, this will consist of pieces parallel to the axis of t (during the intervals mentioned) interchanged by very steep tops of which the maximum ordinate depends on the maximum value of $\left(\frac{\partial\varepsilon}{\partial q_\nu}\right)^2$. During an interval of time, very long with respect to the average time between two successive collisions, the graph will show very many tops of various heights. In a sufficiently long interval the tops of each kind are likely to occur in each part of the path. The time during which the velocity is $\sqrt{\frac{2\varepsilon}{m}}$ shall be the same fraction for every path that is sufficiently long, with deviations which are small in comparison with the quantities themselves. For example the number of tops of a certain kind be N_b for unity of time then we shall find deviations of the order of magnitude of $\sqrt{N_b}$, if we compare those numbers for different intervals equal to the unity of time. If now the duration of the collisions and also (e.g. by enlarging n) the average time between successive collisions approaches 0, but in such an way that the first is infinitely small compared with the second, then the (v-t) graph will show an infinity of maxima and minima in a finite region.

In the second extreme case a large number of points differing widely in phase, will always be in collision with the walls. If the number of collisions of the given phase is N pro unity of time then deviations of the order $\sqrt{N}$ (positive as well as negative) will occur. The length of the path through which the system passes on the line L in a unity of time will be the same for the majority of suchlike intervals. The square root of the mean square of the deviations is small in comparison with the length of the path itself.

Let us next consider a system in which n perfectly rigid and elastic spheres of diameter σ are enclosed in a volume V. We fix our attention on a line-ensemble. The points of the line represent the phases of the system. In some of them the number of particles for each of the k equal elements V_λ into which the volume V may be divided will be exactly $\frac{n}{k} = \nu$; in others there can exist deviations which I shall indicate by τ_λ for the element V_λ. The numbers τ_λ answer to the condition $\sum\limits_1^k \tau_\lambda = 0$. I shall assume the elements V_λ great in comparison with the mean length of free path (of the molecules). Then a distribution with certain values of the numbers τ_λ will last for some time. We can therefore take rather long parts of the path L so that on each of them the value of τ_λ may be considered to remain constant. Let l be a part in which no deviations occur, l' another with the deviations τ_λ.

We have to determine

$$\sum_1^n \left(\frac{\partial \varepsilon}{\partial q_\nu} \right)^2$$

on those parts of L.

The sum will show irregular deviations from one moment to another, caused by the accidental variations of the number of collisions. The mean value however can easily be denoted, it is different for l and l'. The contribution to the value will depend for each element on the number of collisions occurring in the unity of time.

Applying the known elementary theory of mean free path we have to put this number proportional to $(r + \tau_\varkappa)^2$. If we admit that all possible configurations still occur in a large number, we can put for the contribution of the $\varkappa^{th}$ element to the velocity

$$\alpha (r + \tau_\varkappa)^2$$

The coefficient α depends on the nature of the forces in the collisions. We therefore find for $\sum\limits_1^n \left(\frac{\partial\varepsilon}{\partial q_\varkappa}\right)^2$ in the system in question:

$$\alpha \sum_1^k (r + \tau_\varkappa)^2$$

and for the velocity

$$v_\tau = \frac{2\varepsilon_p}{m} + \alpha \sum_1^k (r + \tau_\varkappa)^2 .$$

For the system with equal but opposite deviations we find:

$$v_{-\tau} = \frac{2\varepsilon_p}{m} + \alpha \sum_1^k (r - \tau_\varkappa)^2 .$$

Taking into account that $\sum\limits_1^k \tau_\varkappa = 0$, we find

$$v_\tau = v_{-\tau} = \frac{2\varepsilon_p}{m} + \alpha \sum_1^k r^2 + \alpha \sum_1^k \tau_\varkappa^2 = v_0 + \alpha \sum_1^k \tau_\varkappa^2 ,$$

v_0 being the mean velocity for the homogeneous system.

The mean value of velocity for the deviating system is therefore always greater than the one for the homogeneous system. The collisions with the walls are neglected, this is permitted, as their number is much smaller than that of the mutual collisions; moreover their contribution is for long periods of time the same for the three systems. The path through which the homogeneous system passes on in a long time T is $v_0 T$, for the deviating systems $\left(v_0 + \alpha \sum\limits_1^k \tau_\varkappa^2\right) T$, the deviations of these values being small compared with the values themselves. So the path is smallest for the most frequently occurring system and equal for deviating but equally probable systems.

Chemistry. — "*Investigations on the radium content of rocks.*" II.

By Dr. E. H. Büchner. (Communicated by Prof. A. F. Holleman).

As a second contribution to the knowledge of the radium content of the earth's crust,[1] I now wish to communicate the results of the measurements of a few sedimentary rocks. I may refer to my previous paper for particulars about the method of investigation; only the way, in which the substance was brought into solution, may be briefly exposed. It was much shorter than in the case of igneous rocks, because the investigation has been limited to rocks which dissolve for the greater part in dilute hydrochloric acid. I took, as usual, twenty-five grammes of the finely powdered rock and dissolved, gently heating, in 250 c.c. dilute hydrochloric acid. A usually small residue was left, which, after having been separated from the solution, was fused with a little sodiumcarbonate. Leaching with water gave a solution, in which in all cases sulfuric acid could be detected. The presence of radium being hereby excluded, I rejected this liquid, and dissolved the very small residue of carbonates in a few drops of hydrochloric acid. This solution was mixed with the main solution, which then was measured in exactly the same manner as described in my previous paper. During the course of the measurements I have for the sake of security regauged the electroscope, using the radiumbromide solution of Professor Rutherford; I obtained exactly the same value as formerly.

The investigation concerns four samples of marble, six of limestone, chosen from different geological periods and one of chalk; fresh specimens of the rocks were supplied to me by Dr. F. Krantz of Bonn.

The results are given in the following table, in which the figures relate to the quantity of radium per gramme of rock, expressed in 10^{-12} grammes

Marble		Carrara	1,3
,,		Piasco, Valle del Po.	1,6
,,		Auerbach, Bergstrasse	1,7
,,		Villmar, Nassau	0,8
Limestone,	silurian	Kuchelbad, Prag	0,7
,,	carboniferous.	Ratingen, Düsseldorf	4,3
,,	trias	Jena	0,4
,,	lias	Vaihingen, Württemberg	2,1
,,	lower chalk	Egestorf, Hannover	0,3
,,	eocene	Paris	0,8
Chalk diluvial		Pietersberg, Maastricht	1,5

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[1] These Proceedings XIII, 359 (1910).

It is seen, that, if we disregard the sample from the carboniferous formation, the numbers do not differ much, at least less than was found for igneous rocks. We do not observe either any relation between radium content and geological age: the figures in the table are distributed arbitrarily. The same holds for the four specimens of marbles; the two first are geologically more recent than the last, but a corresponding difference in the quantity of radium present is not to be found. The general mean of the above numbers is 1,4 and agrees fairly well with the mean, which can be calculated from different (in all ten) values, given for limestone by STRUTT [1]), EVE [2]), COLERIDGE FARR and FLORANCE[3]), SCHLUNDT and MOORE[4]) and which amounts to 1,3. On the contrary a much higher mean of 3,3 would follow from JOLY'S [5]) data, which relate to twelve rocks of this kind. We cannot yet settle the question, whether this difference must be ascribed to chance or is caused by the small deviations between the methods of determination. In this connexion, though, I must draw attention to the fact that JOLY, measuring a limestone from Vaihingen obtained the value 3,0, while in my table the number 2,1 is found; this would tend to make influence of the method of working more probable.

In conclusion I would like to make a remark on the often expressed opinion that sedimentary rocks contain generally less radium than igneous ones do. As a matter of fact, the mean of all sedimentary rocks measured is less than that of the igneous, but, if we divide the last into groups, it becomes evident, that this difference is only caused by the high radium content of the granites, whilst the fact, that an especially great number of samples of this rock have been measured, tends to make the general mean higher. If we calculate e.g. the mean of the ten results, obtained by FARR and FLORANCE and by FLETCHER [6]) for trachyte, we obtain 1,0, a lower value than that given above for limestone. Such a result will probably be also obtained for other igneous rocks; I hope to return to this subject later on, after having measured further samples of these rocks.

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[1]) Proc. Roy. Soc. A **78**, 150 (1906).

[2]) Phil. Mag. [6] **14**, 231 (1907).

[3]) Phil. Mag. [6] **18**, 812 (1909).

[4]) U. S. Geological Survey, Bulletin 395 (1909).

[5]) Radioactivity and geology, London 1909, p. 60.

[6]) Phil. Mag. [6] **20**, 36 (1910).

Chemistry. — *"On the action of nitrous acid on dinitrodialkylanilines"*. By Prof. P. van Romburgh.

According to Hantzsch (B. **43**, 1674 [1910]) there is formed by the action of nitric acid (D. 1.3) on dimethylaniline, 3.4 dinitrodimethylaniline which is regarded by him as a new compound. Apart from the fact that I obtained this substance many years ago (Rec. VI, 253 [1887]) and explained its structure in 1895 [1]), the communication of Hantzsch attracted my attention because in my investigations as to the action of nitric acid of widely different concentrations on dimethylaniline, I always obtained — dependent on circumstances — besides tetranitrotetramethylbenzidine [2]), derivatives of mono- and dimethylaniline in which the nitro groups occupied in regard to the amino group, the *ortho* or *para*-position, but never the *meta*-position. Derivatives with a nitro group in the *meta*-position could only be obtained by nitrating dimethylaniline in the presence of a large excess of strong sulphuric acid.

I therefore, have had the action of nitric acid (D 1.3) on dimethylaniline repeated by one of my students, Mr. Jansen. As one of the reaction products there is formed indeed a yellow substance (m. p. 175°—176°) which, however, is nothing else but the well known 2.4 dinitromonomethylaniline, as was shown from the analytical results, and also by a comparison with a preparation obtained by oxidation of 2.4 dinitrodimethylaniline, and with one obtained from methylamine and bromodinitrobenzene with which it did not cause a depression of the melting point.

On the other hand when it is mixed with the 3.4 dinitrodimethylaniline (m. p. 176°) previously obtained by me, it causes a strong decrease of the melting point.

As in the reaction described nitrous acid is generated, it is obvious to assume that by its action on the dimethylamino-group one methyl-group is split off, a reaction of which, moreover, many instances are known.

If to the nitric acid (D. 1.3) a little urea is first added to remove any nitrous acid generated, the monomethyl derivative is not formed, but as main product 2.4 dinitrodimethylaniline (m.p. 87°) is obtained.

In an experiment where a solution of dimethylaniline in ten times its volume of nitric acid (D. 1.3) had stood over night, there was

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[1]) Meeting Febr. 23, 1895.

[2]) Rec. **5**, 244 [1886].

obtained, besides the monomethyl derivative, a quantity of 2.4 dinitrophenylmethylnitrosamine.

That, in conjunction with the results of the nitration experiment in the presence of urea, we may explain the reaction in this way, viz. that first of all the nitrated dimethyl compound is generated, and that this is then converted by the nitrous acid (which is formed by the oxidising action of the nitric acid) into the monomethyl compound (or the nitroso derivative, respectively) is very probable, but by no means certain. Experiments are still in progress to establish this. In the meantime, I have studied the action of nitrous acid on some of the dialkyl derivatives of dinitroanilines.

If we dissolve 2.4 dinitrodimethylaniline in 5 times its weight of nitric acid (D. 1.3) and then add to that solution sodium nitrite until it acquires a strong odour of nitrous acid, a pale yellow compound crystallises, which melts at 86° 1) and is identical with the 2.4 dinitrophenylmethylnitrosamine prepared according to Stoermer 2)). On boiling with acetic acid, the nitrogroup is replaced by hydrogen and we obtain the 2.4 dinitromonomethylaniline (m.p. 176°). With 2.4-dinitrodiethylaniline the reaction proceeds in quite an analogous manner. 2.4 dinitrophenylethylnitrosamine 3)) (m.p. 52°) is formed which also readily loses NO by boiling with acetic acid, and yields 2.4 dinitroethylaniline (m.p. 114°).

2.4 dinitrodipropylaniline 4)) is also converted by nitrous acid into a nitroso compound from which, by means of boiling acetic acid, the dinitromonopropylaniline (m.p. 97°) may be again obtained.

In the dialkyl derivatives of 3.4-dinitroaniline an alkyl group is also eliminated by nitrous acid. If, however, we carry out the reaction in a nitric acid solution (D. 1.3) it is accompanied by a further nitration because, as it seems, the nitrous acid accelerates the nitrating action of the dilute nitric acid.

If, however, we work in a sulphuric acid solution (1 vol. of acid, 1 vol. of water) a nitrosomonoalkyl compound is formed even with these derivatives.

With 3.4-dinitrodiethylaniline, for instance, a beautiful pale yellow nitroso derivative (m. p. 79°—80°) is formed from which the nitroso

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1) It is sometimes contaminated with the non-nitrosated monomethyl compound. It will be ascertained whether this is formed primarily, or by the action of the nitric acid on the nitroso compound. Compare Stoermer loc. cit.

2) B. **31**, 2530 [1898].

3) Stoermer loc. cit. pag. 2531.

4) This compound which I described fully 20 years ago (Rec. **8**, 252 [1889]), is described in Hantzsch's paper loc. cit. p. 1675 as a new one.

group is split off by boiling with phenol or acetic acid. The 3.4-dimethyl derivative also reacts readily with nitrous acid in sulphuric acid solution; the compound formed is still under investigation.

Finally, I have allowed nitrous acid to act on the dark red 3.6-dinitrodiethylaniline (m. p. 76°) when a beautiful pale yellow nitroso compound (m. p. 69°) is formed, which on being boiled for a moment with acetic acid, yields on dilution with water beautiful red needles of the 3.6-dinitromonoethylaniline (m. p. 120°) previously described by me, so that in this case also one of the ethyl groups has been eliminated. The 3.6-dinitrodimethyl compound behaves in quite an analogous manner, just like p. nitrodiethylaniline.

These experiments are being continued with other tertiary nitrated amines.

Utrecht. *University Org. Chem. Lab.*

Chemistry. — "*Confirmations of the new theory of the phenomenon of allotropy.*" I. By Prof. A. Smits and Dr. H. L. de Leeuw. (Communicated by Prof. van der Waals).

(Communicated in the meeting of December 24, 1910).

As was set forth before[1]) the above-mentioned theory leads us to expect that for every substance which presents the phenomenon of *heterogeneous* allotropy, so *monotropy* or *enantiotropy*, the phenomenon of *homogeneous* allotropy will also occur, because the two phenomena are in the closest connection.

So in virtue of this theory we can expect for the monotropic and enantiotropic substances that every vapour, liquid, or solid phase in stable condition consists of an internal equilibrium between different kinds of molecules. A consequence of this is then that when we make the temperature vary so rapidly that the internal equilibrium cannot keep pace with the temperature, the more complex nature of the substance will appear, which will, among others, manifest itself in a boiling or melting range of temperature, in which the final boiling point, resp. final melting point will lie higher or lower than the unary stable boiling point, resp. melting point, dependent on the type of the pseudo-system and of the direction of the line which indicates the internal equilibrium in the vapour, resp. liquid phase.

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[1]) These Proc. March 1910 p. 763.

As was shown in the preceding communication [1]) on this subject, this has really already been observed in the melting-point determination of the rhombic sulphur.

The first substance that was closely examined by us in this direction was the *white phosphorus.*

Theory has already drawn attention to the fact that not only the *violet,* but also the *white* phosphorus is built up of different kinds of molecules, so that the possibility existed, that the complexity of this metastable modification could be demonstrated.

Experiment has corroborated this supposition, and that so convincingly that as yet no substance is known, by means of which the validity of the theory can be demonstrated in so simple and clear a way as by means of the *white phosphorus.*

Before this result was obtained, however, a great difficulty had to be surmounted, which consisted in the preparation of pure phosphorus.

It appeared, namely, that none of the known methods yielded a product that melted in a unary way also when the supply of heat took place very slowly, i.e. a substance was always obtained which presented a range of melting temperatures.

The melting-heat of white phosphorus being so small (5 cal.), an exceedingly slight quantity of a second substance can already cause an appreciable range of melting temperatures, and it was therefore to be foreseen that the preparation of a product melting at one and the same temperature might present peculiar difficulties.

As it appeared that the last contaminations must chiefly consist in the oxides of phosphorus, which cannot be sufficiently separated from the phosphorus by the usual methods of purification (treatment with potassium dichromate and sulphuric acid, distillation with steam, etc.) an apparatus was constructed (fig. 1), in which the phosphorus was distilled in vacuo, and then subjected to a repeated partial crystallisation, after which it was transferred, thus purified, to a melting point determination vessel.

The latter is represented in fig. 1 by *A*. A resistance thermometer is sealed to it; this vessel is connected with three bulbs *B*, *C*, and *D*, the last of which (capacity 500 cm.) at first filled with water, was afterwards filled for three quarters with pieces of commercial so-called pure white phosphorus.

After this phosphorus had been melted under water, and had then solidified again, the water was poured off, leaving only a thin layer, and then the tube *d* was sealed.

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[1]) l. c.

Then the tube *c* was connected with the *Gaede-pump* through two U-shaped tubes placed one behind the other.

The first of these tubes was placed in a vessel with solid carbonic acid and alcohol to condense all the water-vapour, the second being immerged in a vessel with liquid air to solidify the last traces of phosphorus so that a high vacuum could be obtained.

Now first of all the apparatus was exhausted, and the flask *D* was carefully heated with the flame to distill off the water.

When nothing of the water was to be detected any more we continued the boiling in vacuo for another half hour to be sure that also the water dissolved in the phosphorus was entirely removed.

After the connection of the apparatus with the pump had been broken by sealing it at *b*, three fourths of the phosphorus was distilled over into *B*, in which a liquid was obtained, which at first opalized somewhat, but became perfectly clear and colourless afterwards.

Though this phosphorus appeared to be as pure or purer than the purest product obtained by other methods, it was not yet pure enough for our purpose, as experiment showed that this phosphorus could not be made to melt sharply at one temperature by any means whatever.

To reach a still higher degree of purity the phosphorus in *B* was almost entirely melted, and then made to crystallize again by slow cooling; when three quarters of the mass had solidified, the remaining liquid was conveyed to *C* by tilting of the apparatus, and solidified there by strong local cooling of the supercooled liquid (by means of solid carbonic acid and alcohol).

This manipulation was repeated a great many times, in which the mass remaining in *B* did not only get continually a higher melting-point, but also became coarser and more perfectly crystalline.

When through this repeated partial crystallisation and removal of the liquid four fifths of the quantity originally present in *B* was conveyed into *C*, we filled the vessel *A* with the phosphorus which had remained in *B* by melting it in *B*, and by then making it flow into *A* by tilting the apparatus.

By then sealing off at *a* we broke the connection of the melting-point-vessel with the other part of the apparatus, and the experiment could begin.

The perfectly colourless coarsely crystalline phosphorus obtained in this way now appeared te be so pure, that on immersion of the melting point-vessel in a thermostat the temperature of which varied slowly, a melting-range was found smaller than 0.02°, so that we may say that we have determined the unary melting-temperature of the white phosphorus, for which we found 44,0°. Here we must remark however that only the differences of temperature are exact to one hundredth of a degree; the absolute values of the temperature may perhaps need a small correction, as we used as a standard of temperature a thermostat which had the temperature of 44° according to a controlled normal thermometer.

When it had thus been proved that the phosphorus obtained by us has the property of melting resp. solidifying in a unary way, it was examined in how far the complexity of the phosphorus betrayed itself when we worked rapidly.

As the result can be most clearly demonstrated by curves of cooling resp. of heating, we shall successively discuss figs. 2, 3, 4, and 5, which will give us a highly interesting insight into the inner nature of the white phosphorus.[1]

Fig. 2 refers to the following experiment: the meltingpoint vessel with white phosphorus was kept in a thermostat of 40° for a day, and then suddenly transferred to a bath of 50°, after which the temperature was read every 10 seconds by means of the galvanometer in a WHEATSTONE bridge. Now it follows from the curve in fig. 2, which indicates the temperature as a function of the time, that the melting set in at **43,92**°, and was completed at **43,96**°.

The small range of melting temperatures of 0,04° shows that the substance behaved in an almost unary way, but not perfectly so, which is owing to this that the internal equilibrium had set in at 4° under the unary melting-point.

In another experiment another course was taken. The melting-point-vessel was kept for some time in a bath of ± 46°, and then taken from the bath to make the cooling take place under exposure to the air.

As the phosphorus is very easily supercooled, the crystallisation had to be started by grafting. For this purpose the capillary point *e* of the meltingpoint-vessel was for a moment brought in contact with solid carbonic acid and alcohol, when the temperature of the

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[1] In Fig. 2 the curve begins to rise more slowly at 42°, because melting occurs already in the outer layers of the phosphorus, which are warmer than the layer in contact with the thermometer. If this was not the case, we should have got the dotted line and melting would not have appeared before 43.92.

At *c* the curve begins to rise more rapidly because the heterogeneous equilibrium no longer sets in rapidly enough — in consequence of the small quantity of solid substance present — that the heat applied to the solid substance is consumed entirely in melting it. If this had been the case, the course would have been also here as the dotted line indicates and the melting would have been completed at 48°.96.

phosphorus had fallen below 44°, in consequence of which immediately solid phosphorus formed in the capillary, which started the crystallisation of the large mass, during which the temperature rose in consequence of the heat of solidification.

The curve representing the result of this experiment has been drawn in fig. 3. In this fig. *a* denotes the point where the grafting took place. Then the temperature fell to *b*, after which it rose to *c*, then it descended at first very slowly, then all of a sudden very rapidly. The result is that also in this way of working the phosphorus solidifies in an almost unary way, for the interval of solidification amounts only to 0,05°, but in consequence of the comparatively large difference of temperature with the surroundings the unary melting temperature was no more to be reached.

In a third experiment which yielded a very important result, the meltingpoint-vessel was first placed in boiling water for some time, and then suddenly transferred to a bath of 15° to make the cooling take place so rapidly that the internal equilibrium could certainly not keep pace with it. When then grafting took place at about 43°.5 after taking out of the bath, the temperature rose above 44°, from which, therefore, followed that *when the cooling takes place very rapidly the liquid phosphorus is already supercooled above* 44°.

Therefore another time the grafting took place *above* 44°, when the temperature rose to 45°.5, and we succeeded in getting a rise of temperature to 46° with still earlier grafting, which, however, is by no means the highest temperature to which the phosphorus can rise in this way.

The curve of cooling, obtained in one of these experiments, is represented in fig. 4, and it is noteworthy how much this curve, which is the result of a perfectly analogous experiment to that to which fig. 3 relates, apart from the previous history of the phosphorus, differs from the curve in this last figure. The grafting took place above 44° at about 44.°5; at first the temperature descended, then it rose to 45°,05, after which it fell again, at first pretty rapidly, then less rapidly and at last very rapidly again.

The whole line shows the type of a line of solidification of a mixture, the melting-range is here about 1°.8, but can be considerably larger still, which already follows from this that in one experiment a temperature maximum was observed of 46°.

That the phosphorus which has been ill-treated in this way, and at first unites to a *distinctly visible conglomerate* in the solid state tries to reach internal equilibrium pretty rapidly, follows from fig. 5. The curve traced in this figure is, namely, a curve of heating, which shows what has been observed after the solid substance obtained in the previous experiment has been suddenly placed in a bath of 50°. The curve of heating now shows that after some minutes a considerable approach to the state of internal equilibrium has taken place, but it has not been reached as yet, for the melting-range still amounts to 0°.13, and the end-melting point lies above the unary melting-point temperature.

Before proceeding to an interpretation of the observed phenomena, we may point out here that, as CHAPMAN [1]) found that red P melts to a perfectly colourless liquid, it has already been assumed in the preceding communication, that the line for the internal liquid equilibrium runs to the side of αP with rise of temperature [2]). If we do so again here we are obliged, in contradiction to the T,X-figure given before, to draw a eutectic point in the pseudo-binary system, as has been indicated in fig. 6, because only in this case the observed phenomena can be explained [3]).

The line kl_2l_1 denotes the internal equilibria in the liquids, and s_1n refers to the internal equilibria in the solid white phosphorus, so that s_1 and l_1 indicate the solid and the liquid phases which are in internal equilibrium, and coexist at the unary melting-point of the white phosphorus.

Now it follows from the course of the mentioned lines of equilibrium, that when the liquid l_0 is cooled very rapidly, the crystallisation can already occur at l_1. Then in the absence of internal transformations a melting-range $l_1 l_1$ would be found, whereas in case of rapid heating of the solid phase n the melting will already begin at s'_2, and be completed at l'_2, namely in case there are no internal conversions at all. The internal conversions, however, especially when the two phases S and L are in contact, proceed with fairly great rapidity, and this is the reason, that a transgression of the unary melting-point temperature is always much smaller than the lines $l_1 l'$, and $S'_2 l'_2$ would lead us to expect.

Further the figure shows that the initial solidification resp. the initial melting will appear the sooner according as a higher resp. a lower temperature is started from, and thus we see that the new theory of allotropy, given in our preceding paper, gives a natural explanation of the observed phenomena [4]).

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[1]) Journ. chem. Soc **75**, 743 (1899).

[2]) zP is a substance we do not know, but of which we may assume with a high degree of probability, that it is colourless.

[3]) It follows at the same time from this, that we have not to deal with the phenomenon of polymerism for the phosphorus (see preceding communication).

[4]) Rapid heating, from low temperatures, gives only a small change; so the line ns_1 has a rather steep course.

We may finally remark here that JOLIBOIS[1]) thinks he has shown with certainty that there are not *two* but *three* solid modifications of the phosphorus, *white*, *red*, and *pyromorfic* phosphorus, which last we shall call *violet* phosphorus, as is more rational.

As JOLIBOIS remarks it would also follow from his investigation that the violet P is stable under 460°, above it, however, the red modification, which melts to a colourless liquid at 610°.

When we accept these results it is the question how we can account for the behaviour of the phosphorus in the light of the new theory.

We might suppose that if three different solid modifications exist of a substance, these three forms would have to be ascribed to the existence of three different kinds of molecules.

This view has, accordingly, been advanced in the first communication, but if we think of substances with three, four, or more points of transition, this supposition is somewhat improbable, and as it proves on further consideration not to be necessary, we prefer another simpler and more plausible supposition for the present.

Also for the case that a substance occurs in three crystallized modifications, the existence of two kinds of molecules can account for the phenomena, namely, when we assume a second discontinuity in the series of mixed crystals.

This has been done for the phosphorus in fig. 6; we see that the liquids bl coexist with the mixed crystals bs', the liquids lc being in equilibrium with the mixed crystals se.

In this figure s_2 represents the red phosphorus at the unary melting-point temperature. Below this temperature, which lies at 610° according to JOLIBOIS, the red phosphorus remains stable to 460°, at which the red modification, which is denoted by s_3, is converted to the violet S_4, which is therefore stable below 460°.

We may further remark that as red P is obtained on a manufacturing scale from yellow P by heating to 280°, the line l_2l_1 must be left and the line $s_3s'_3$, reached, which however, is also still metastable, and that then, as JOLIBOIS found, by means of the catalytic agent *Iodium*, the stable state at that temperature, the violet P is obtained, which lies on the line s_4q.

The second substance which was examined as to its complexity, was mercury. As only one crystallised state is known of this substance, and as not one of its properties betrays a complex character,

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[1]) Comptes Rendus **149,** 287 (1909).
„ „ **151,** 382 (1910).

it was supposed that this substance would always behave in a unary way. Experiment has fully confirmed this conjecture. Whether mercury was suddenly cooled by water in vacuo from ± 300°, and then by solid carbonic acid and alcohol, or whether it was rapidly heated from 80°, the point of solidification, resp. melting-point always remained the same, and the substance perfectly behaved as a unary one, from which we may therefore draw the conclusion that when the substance is complex the internal transformations must proceed with extraordinarily great rapidity, or what is more probable that mercury really consists of one kind of molecules.

The third substance examined by us, for which in view of its transition points, the same was expected as for the phosphorus, was tin.

Though the investigation made bears as yet still a preliminary character, we may yet communicate that tin of particularly great purity can solidify entirely as a unary substance, but that it betrays its complex character when the experiment is made very rapidly, just as phosphorus does. In a following communication we hope briefly to communicate the result of the final investigation.

Amsterdam, December 23rd 1910.

Anorg. Chem. Lab. of the University.

Chemistry. "*On the determination of threephase pressures in the system hydrogen sulphide + water.*" By Dr. F. E. C. Scheffer. (Communicated by Prof. A. F. Holleman).

1. In the investigation of the systems in which hydrogen sulphide is one of the components, the difficulty presents itself that a chemical action can affect the mercury that shuts off the mixture, when it is not sufficiently purified from admixtures. This action will chiefly be due to the presence of slight quantities of air. By excluding the presence of air (and water), as completely as was possible in the methods used, I succeeded before in determining the situation of the three-phase curves in the system hydrogen sulphide + ammoniac. The methods used in the investigation, had to be adapted to high pressures, as it was my principal aim to determine the points of intersection of the critical line and the three-phase curves, the critical end-points. In this I have at the same time found an opportunity to determine the shape of the spacial figure of the mentioned system at lower temperature; the observations at these low tempe-

ratures and the low three-phase pressures corresponding with them though perfectly sufficient qualitatively, could of course lay claim to but little accuracy, particularly because the pressures were read on a metal manometer, which indicated up to 250 atmospheres, and which can give only rough values below about 20 atmospheres, and because the slow setting in of equilibrium can cause a great relative error at these low pressures.

I have now tried to find an improved method for the investigation at pressures below 20 atmospheres, which could yield more accurate results. I intend to give here a description of this method and to demonstrate its efficiency not by the aid of the system hydrogen sulphide + ammoniac, as this would only involve a repetition of former observations, which would not open new vistas [1]), but apply this method to another system with hydrogen sulphide as component, namely the system hydrogen sulphide + water. As will appear from the following description, mercury is not affected by moist hydrogen sulphide, at least below 30°, when presence of air is carefully excluded.

2. *Preparation of the mixtures.*

For the preparation of a hydrogen sulphide + water mixture the

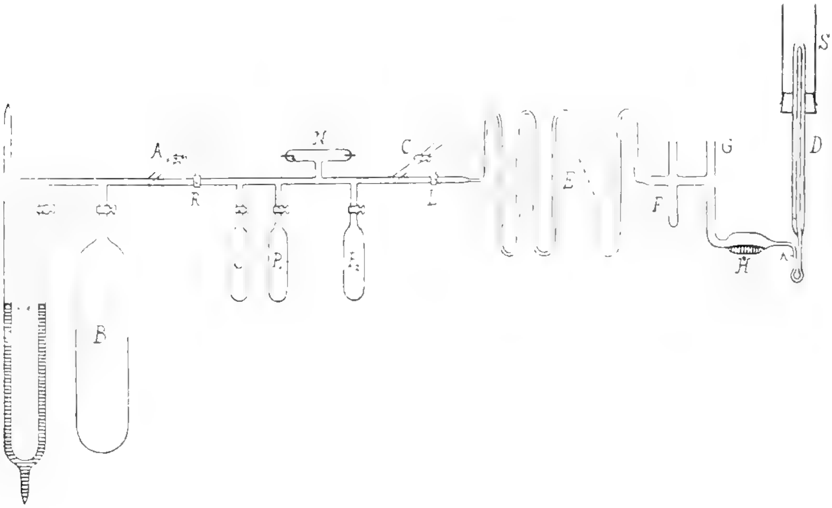

Fig. 1.

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[1]) These observations will shortly appear in the Zeitschrift für physikalische Chemie. It may only be remarked here that action of hydrogen sulphide on mercury was no longer observed, and that e.g. reduction of the volume under three-phase pressure to half its size, gave an increase of pressure, which generally amounted to less, but in one case to slightly more than 0,1 atmosphere; these deviations are about as great as the errors of observation.

apparatus was used, represented in figure 1. The hydrogen sulphide was prepared from a solution of natrium sulphide, which was free from carbonic acid and diluted sulphuric acid; the former solution was obtained by saturating natron, which had been freed from its carbonic acid by the addition of barium hydroxide, with hydrogen sulphide. The gas prepared in this way was dried by phosphoric anhydride, and led into the exhausted vessel *B* through the cock *A* (fig. 1); it was then freed from air by condensation in *O* by means of the two vessels P_1 and P_2, which were filled with carbon of cocoa-nut; *O*, P_1, and P_2 had been placed in liquid air for this purpose. If now there were no discharges at all in the GEISSLER tube *N*, the hydrogen sulphide was again conveyed from *O* into the reservoir *B* by evaporation. Then the gas which had remained in the tubes of the apparatus between *M* and *L* could be sucked off by means of a water-jet-pump, when the cock *C* was opened.

The Cailletet tube, which was made of common glass for this experiment, where the pressures did not exceed 25 atmospheres, and which could have a comparatively large bore (5 mm.), was sealed to a glass spring *E*, and thus connected with the apparatus.

Now a quantity of mercury freed from air by boiling which was sufficient to fill the entire test-tube *D*, was brought into the reservoir *H* through *G*. After *G* had been sealed, *F* was provided with a little distilled water, and the upper end of this tube was also sealed. Now the water in *F* was frozen, and the test-tube was evacuated by means of the water-jet-pump (cock *C*) and carbon (F_1 and P_2). After the cock *L* had been closed, the water could now be distilled over from *F* to the upper end of the test-tube, which had been cooled with liquid air (vessel *S*).

A quantity of hydrogen sulphide was admitted from *B* into the apparatus between *M* and *L* with open vessel *O*; by means of the manometer *M*, whose rightside leg had been evacuated, this quantity could be roughly estimated. This gas too was solidified in the upper end of the test-tube when *L* was opened.

When I had then convinced myself that no air was present in the test-tube (discharge in *N*), the Cailletet tube was tilted, in consequence of which the mercury flowed from *H* into the *U*-shaped lower end of the test-tube, and was forced up to the top of the test-tube by the air in consequence of the opening of the cocks *C* and *L*. Now the Cailletet tube was separated from the apparatus at *K*, and placed in the pressure cylinder which was filled with mercury purified and freed from air by boiling.

When we work in this way the presence of air is practically excluded and the mixture is only in contact with a small quantity of pure mercury; so contact with not entirely air-free mercury and rubber joints are entirely avoided in this way.

3. *Determination of pressure and temperature.* A cylindric vessel conically narrowed at the lower end was fastened to the Cailletet-tube by means of a cork, and filled with water. The heating took place electrically; the temperature was regulated by means of an incandescent lamp resistance, and read on an Anschützthermometer, which had been compared with a normal thermometer. The stirring took place in the waterbath by means of lead plates, which moved vertically up and down, in the test tube by means of a KUENEN stirrer; the electromagnetic coil required for this was vertically moved round the heating-vessel.

For the determination of the pressure I used two air-manometers, one of which indicated a minimum pressure of about 3, the other of about 8 atmospheres. The errors of the method remain in this way below 0°.1 and 0.1 atmosphere (errors of the manometer and difference of position between the mercury in the test tube resp. manometer and in the pressure cylinder); the errors which can be made in the determination of the three phase curves, may be generally estimated at about 0.1 atmosphere, as appears from the concordance of the results. I shall, however, return to this, when discussing the results.

4. *Results.* In fig. 2 the *P-T*-projection of the spacial figure is represented. In the first place we see drawn in it the vapour-pressure curve of hydrogen sulphide, which had been determined before by many observers. Just as in my previous determinations concerning the system hydrogen sulphide + ammoniac I arrived again at the result that the values given by REGNAULT, are too high; in the range of temperature investigated by me the deviations vary between 0.8 and more than one atmosphere. The only value which was determined by OLSZEWSKI in the range examined by me, presents a deviation of less than 0.1 atmosphere from mine, and has been denoted by *O* in the graphical representation; REGNAULT's deviating values I have omitted in the figure for the sake of clearness.

The hydrogen sulphide showed a variation of pressure of less than 0.1 atmosphere on isothermal compression to a fourth of the total volume, while also the pressure at which the last quantity of vapour disappeared differed less than 0.1 atmosphere from that at the greatest possible volume.

Immediately below this line two three phase curves appear in the *P-T*-projection, one of which indicates the coexistence of the hydrogen sulphide hydrate by the side of vapour and a liquid rich in hydrogen sulphide, and the second the equilibria between two liquid layers and vapour. The former three-phase curve (SL_1G) gives

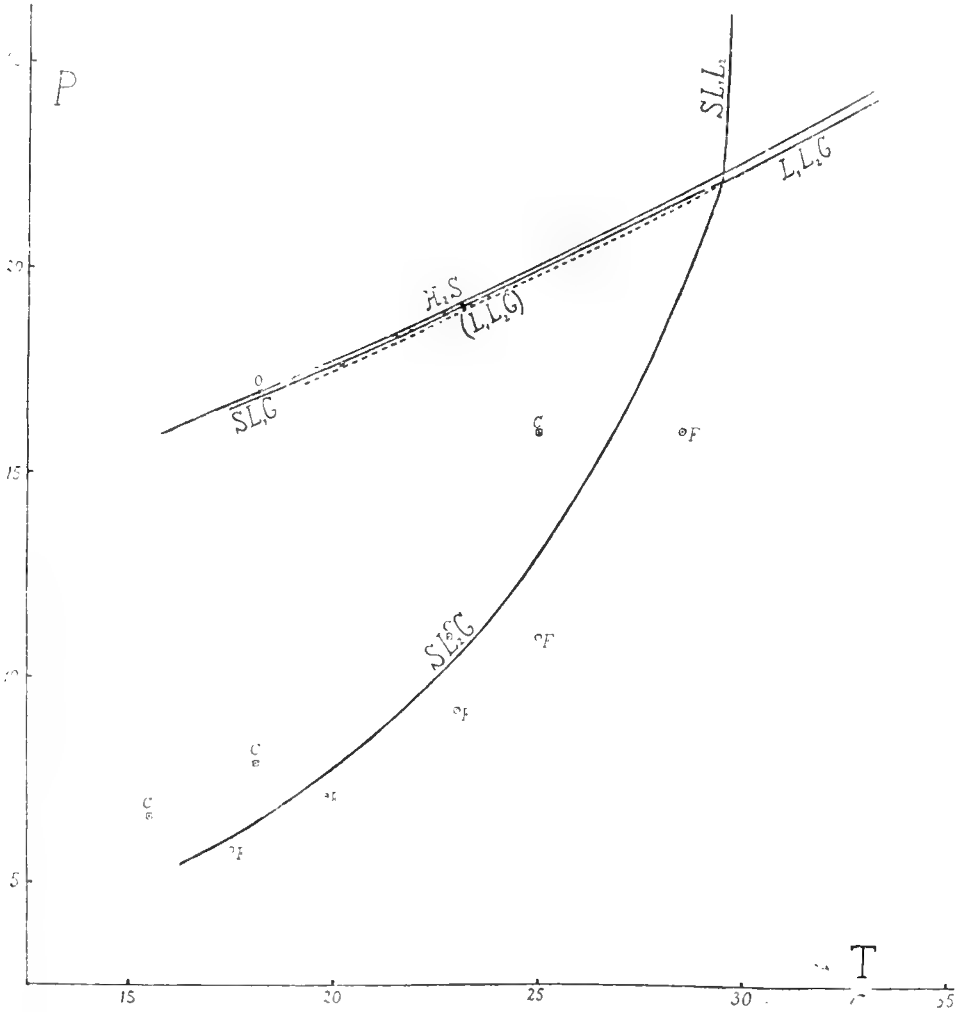

Fig. 2.

stable states all over its course; the other (L_1L_2G) metastable states below 29.5°, above this stable equilibria. The isothermal differences of pressure between these two three-phase curves and the above-mentioned boiling-point curve of hydrogen sulphide, are very slight, and are near the errors of observation, as regards their order of magnitude. Still I think I am justified in concluding with certainty from the great number of observations given in the table that the pressures are greater on the three-phase curve SL_1G than on L_1L_2G, and that the boiling-point line of hydrogen sulphide lies higher than either.

Also looked upon from a theoretical point of view this order seems the most probable one; for if the liquid-vapour surface of the hydrogen sulphide continually descends to the side of the water, the three-phase pressures will lie below the maximum tension of liquid hydrogen sulphide at a certain temperature, and (below 29.5°) the metastable $L_1 L_2 G$ curve will have to lie lower than the stable $SL_1 G$-curve. We can see this, among others, already from this that for the coexistence $L_1 L_2 G$, the liquid L_1, being metastable, must be super-saturate with respect to the hydrate, and so richer in water than the liquid L_1 on the three-phase curve $SL_1 G$.

$LG\,(H_2S)$			L_1L_2G		SL_1G		SL_2G		
T	P	P	T	P	T	P	T	P	P
15		16.38 R							
15.8	15.9+		19.4	17.3	17.4	16.6	15.5		6.6 C
15.9	16.0—; 16.0+		19.8	17.4	18.4	17.0—	16.3	5.3—	
16.0	16.0		20.6	17.8—	18.7	17.05	17.5		5.8 F
16.2	16.1		20.8	17.9—	19.0	17.2	17.9	6.3—	
17.0+	16.5-		21.2	18.0; 18.0	19.9	17.6—	18.4		7.9 C
17.6	16.7		21.4	18.15; 18.2	20.9	18.0—	19.7	7.6	
17.8	16.8—; 16.8—		22.8	18.85	21.2	18.1+	19.8		7.1 F
18.2		16.95 O	23.0	18.95	21.8	18.4+	21.0	8.6+	
19.0	17.3—		23.65	19.3—	22.9	18.9+	22.8		11.0 C
20		18.62 R	24.6	19.7+	23.65	19.3	23.0		9.2 F
20.4	17.9+		24.8	19.85; 19.8—	23.8	19.35	23.3	10.7	
21.2	18.25		25.1	20.0—	24.1	19.5+	24.8+	12.9	
22.0	18.65		25.4	20.0—	26.0	20.5	25.0		11F; 16C
23.6	19.4+		25.6	20.1—	26.6	20.7—	25.6	14.0—	
24.9	20.0+; 20.1—		25.8	20.2; 20.3—	27.2	21.0+	27.4	17.1	
25		21.07 R	26.4	20.6	27.3+	21.05	28.5	19.5+	16 F
25.4+	20.3—		26.9	20.75	28.2	21.5+	29.2	21.3+	
25.8	20.5—		27.5	21.0+	28.8	21.8			
26.1	20.6+		28.0	21.3—	29.4	22.1			
26.2	20.7—		28.2	21.4					
27.5	21.3		28.4	21.5+					
29.6	22.35		29.1	21.75					
30		23.73 R	29.2	21.9—					
30.6	22.9		30.3	22.45					
31.6	23.4+		31.0	22.9—					
31.6+	23.45		31.2	22.9+					
33.4	24.45		32.0	23.4					
			32.7	23.8+					
			33.2	24.0+					

SL_1L_2	
T	P
29.8	32

Quadruple point
T 29.5 ; P 22.1 +

R = Regnault
O = Olszewski
C = Cailletet and Bordet
F = de Forcrand

The possibility that on the liquid-vapour plane a line of maximum pressure occurs, cannot be excluded beforehand, of course, more especially because in this system a compound occurs, and moreover, one of the components (H_2O) is certainly abnormal. It seems even still possible here, that immediately on the hydrogen sulphide side such a line of maximum pressure occurs; then it must lie, however, at concentrations which are smaller than the gas and liquid concentrations on both the three-phase curves. This, however, does not seem probable for the present, and so I have not taken it into consideration in the P-x-section (fig. 3).

The two three-phase curves SL_2G and L_1L_2G intersect in the quadruple point (29.5°; 22.1 atm.); the two other three-phase curves which pass through this point, where resp. solid hydrate occurs by the side of two liquid layers (SL_1L_2) and by the side of vapour and liquid rich in water SL_2G, have also been represented in the graphical representation.

The preceding table gives a survey of the observations of the discussed lines of equilibrium.

5. By the aid of the above data, a P-x-section has been given schematically in fig. 3, which has been drawn through the spacial figure for about 20°. In this we have assumed, as was mentioned above, that the liquid-vapour surface descends continually from the first to the second component; the point a, the maximum tension of liquid hydrogen sulphide lies higher than the stable three-phase curve $S\,L_1\,G$ (b) and the metastable $L_1\,L_2\,G$ (c)[1]. The other equilibrium curves and the regions given in the figure do not call for a further explanation. I will only draw attention to the fact that the hydrate in this section can no longer occur stable below the three-phase curve $S\,L_2\,G$ (d); for with isothermal increase of volume the transformation $S \rightarrow L + G$ occurs on this three-phase curve, in other words, the

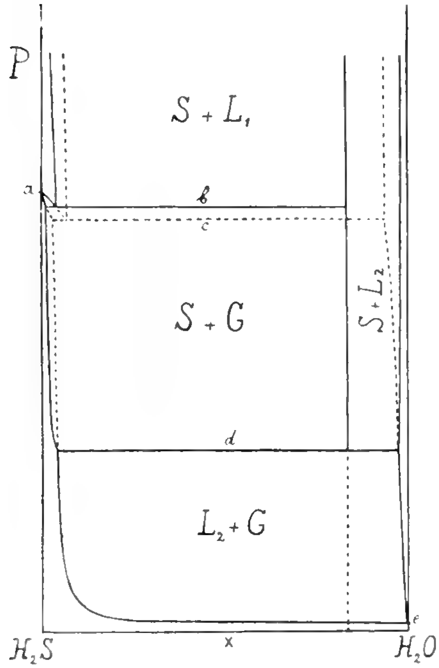

Fig. 3.

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[1] All the metastable lines of equilibrium have been indicated by dotted lines.

hydrate evaporates and melts. Then it will be clear at the same time that the earlier observations of de Forcrand [1]) and of Cailletet and Bordet [2]) refer to this three-phase curve, as they have determined pressures which were necessary for the formation of hydrate; then it becomes also clear that this pressure as de Forcrand points out, is independent of the concentration of the mixture, which is, indeed required for this three-phase equilibrium by the phase rule.[3]) I have indicated their observations by the figures C and F both in the table under $S\,L_2\,G$ and in the P-T-projection of fig. 2. My observations appear to lie between them. The pretty large deviations between the three lines must, in my opinion be ascribed to this, that the formation of the hydrate in case of compression, and the melting in case of expansion takes place slowly; in the first case we find too low, in the second too high pressure. I have made my observations of these three-phase equilibria by slowly heating at constant pressure, and by determining the temperature at which the transformation $S \rightarrow L + G$ occurred. This method of working appeared to yield more accurate results than that in which the transformations were observed for isothermal change of volume.

Whereas the equilibria on the other three phase curves establish themselves spontaneously at constant temperature, and the deviations rarely exceed 0.1 atmosphere, I think I shall have to estimate the accuracy of the observations on the lines SL_2G and SL_1L_2 at 0.1 to 0.2° [1]).

In the P-x-section the gasphase G and the liquid phase L_1 lie on the three-phase-curves on the hydrogen sulphide side; now it appeared from some preliminary experiments that the liquid phase L_2 lies near the water side, in other words that the region of non-miscibility extends over almost the full width of the figure.

Finally a few remarks may be made on the composition of the hydrate. It is not to be derived with certainty from the literature on the subject. De Forcrand, who has made numerous analyses of hydrate, considered successively $H_2S.15H_2O$, $H_2S.12H_2O$, and $H_2S.7H_2O$ the most probable formula. He justly ascribes the very bad agreement of the analysis results to the fact that the hydrate easily

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[1]) de Forcrand. C.r. **94**, 967 (1882); de Forcrand and Villard C r. **106**, 849 (1888).

[2]) Cailletet and Bordet. C.r. **95**, 58 (1882).

[3]) de Forcrand. C.r. **94**, 967 (1882).

[4]) Also the observation of $SL_1\,L_2$ took place by the determination of the temperature at which the transformation $S \rightarrow L_1 + L_2$ is found with slow heating at constant pressure.

retains water. When we further bear in mind that the hydrate is only constant below 0.35° under atmospheric pressure, and that, accordingly, formation of the hydrate at atmospheric pressure without formation of ice will only be possible between 0° and 0.35°, it will be clear that we must here have recourse to special methods of analysis. I shall have to postpone a description of a method suitable for this purpose to a following communication; it may only be mentioned here that even the formula $H_2S.6H_2O$ derived later by DE FORCRAND on theoretical grounds probably still contains too great a quantity of water.

(**February 23, 1911**).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday February 25, 1911.

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Microbiology. — "*Pure cultures from a single cell, isolated under the microscope.*" By Dr. S. L. Schouten. (Communicated by Prof. F. A. F. C. Went).

(Communicated in the Meeting of December 24, 1910).

In 1899 I demonstrated at the Scientific and Medical Congress at Haarlem[1]) a method which I had discovered for isolating a single cell under the microscope, which method, worked out further and applied, appeared in 1901 in these Proceedings[2]) and also formed the subject of my dissertation[3]). Since then I have continued my experiments in this direction. In 1905 I again[4]) published improvements of the method, with further applications and now, 5 years later, the method has again been so much improved and simplified in several respects that I feel a communication should no longer be deferred.

While referring for particulars to my last publication, which, apart from the alterations about to be described, may still serve as description, I wish here to outline the method in brief and then to mention the improvements.

On a coverslip which has been smeared with a little vaseline and then passed through a flame, a drop of the material is placed from which it is desired to isolate a cell. At a distance of about 3 mm. opposite drops are put, in which it is desired to grow the pure culture. The coverslip is then placed on a moist chamber on the microscope stage. The left lateral wall of this chamber is provided with a horizontal slit, which is closed by a viscid fluid and through which a glass needle projects, bent at its end into a loop. By means of a simple mechanism the needle can turn round a support so that its end can touch the lower surface of the coverslip. A mechanical stage renders it possible to do this in any part of the field.

The space in the moist chamber is kept saturated with water vapour by a drop on the floor. The vapour condenses on the lower surface of the coverslip, and since the latter has been treated with

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[1]) Een methode voor het maken van reinculturen, uitgaande van één onder het microscoop geïsoleerde cel". Handelingen v. h. 7e Nederl. Nat. en Gen. Congres, gehouden te Haarlem 1899.

[2]) "On pure cultures of Saprolegniaceeën". These Proceedings March 30, 1901.

[3]) Reinkulturen uit één onder het mikroskoop geïsoleerde cel. Proefschrift. Utrecht 1901.

[4]) Reinkulturen aus einer unter dem Mikroskop isolierten Zelle. Zeitschr. für wiss. Mikr. und für mikr. Technik. Bd. XXII 1905 p. 10.

vaseline, the condensation takes place in small rounded droplets, which do not coalesce. Before use the needle is sterilized in a manner to be hereafter described. A micro-organism to be isolated is now sought at the edge of the so-called material-drop. The needle is moved up so that the end touches the edge of the drop near the cell that is to be isolated.

Then, when the moist chamber is moved sideways the cell with a tiny droplet will be drawn out of the large drop. This cell is now taken up in the eyelet of the needle. This eye is then brought down somewhat so that it no longer touches the coverslip, and then the moist chamber is moved sideways, under a low power, so that the eyelet, by an upward movement, comes near to the edge of one of the sterile drops and deposits the isolated cell, in a small drop, once more on the coverslip

Under the high power this small drop with the cell is moved into the sterile drop, in which the culture is to be made, the so-called culture-drop.

The glass is then placed on an ordinary moist chamber which is kept at the required temperature. If the culture drop is *solid*, then the colony grows on its edge, and with the strongest power its development can be followed from the beginning. If the culture drop is *fluid* the colony generally spreads itself over the whole drop. So much for an outline of the method.

Of the improvements made since my last publication, I mention in the first place, that instead of the isolation apparatus hitherto made by the firm of D. B. KAGENAAR SR. in Utrecht for £ 5 (without needles) I have constructed a simplified arrangement, of which the price with three isolation needles amounts to £ 2. 1. 8. The objection that the needles were not obtainable commercially is thus removed.

Formerly I used one pointed needle, and three ending in an eye: one very small eye of 9 μ in diameter, a medium one of 30 μ, and a large one of 50 μ diameter. Experience has shown me, that the smallest eye, which was the most difficult to manufucture, must be abandoned. It was intended for the isolation of bacteria; with a somewhat greater eye this succeeds much better, and the following 3 needles suffice: a pointed one, an eye of about 30 μ in diameter for bacteria and small yeast cells or spores and an eye of ± 50 μ in external diameter for larger cells [1]).

With the older apparatus there was a needle at each side of the

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[1]) The above mentioned measurements are average values; the diameter and thickness of thread can, without objection, be somewhat larger or smaller.

microscope; with one the cell was isolated, and set down close to the culture-drop, and with the other, i.e. always the pointed needle, the cell was placed in the culture-drop.

The original intention of this was as follows: if it should happen that sometimes a second cell is introduced into the eye of the needle in addition to the one that is to be isolated, this one perhaps might be released unnoticed and could enter the drop together with the cell to be isolated. This mistake can however be avoided if the latter transference to the culture-drop is effected by means of the second needle, which is known to be sterile.

In the meantime I have learnt from experience that in many cases the whole operation can very well be carried out with one needle, in which case the cells of the material must occur so isolated from each other that one cell can easily be taken up without another accompanying it.

On that account the simplified apparatus has only one needle-holder, to the left of the microscope. No *general* rule can however be made, and I intend to return to this later.

In the other arrangement the microscope stands on a plate which can be moved in 4 directions by means of 2 screws: one always begins with the microscope so placed that the needle, when it touches the glass, comes into the middle of the field of vision.

In the simplified apparatus this plate, although convenient in practice, is left out, on account of expense; therefore the miscroscope is adjusted by hand and by tapping with the finger-tip (by which means very slight displacements are obtained).

The needle-holders can be adjusted for microscope stages of various heights.

In the years since my last publication I have gained much other experience which I may add.

Firstly, with special regard to bacteria: one should isolate from material which is as young as possible. Recent experiments have clearly shown that bacteria in a culture very quickly die. The curve of growth which is obtained with the times as abscissae and the bacteria as ordinates, rises quickly and then falls quickly. In cholera, at 37° for example it already reaches a maximum after 12 hours.

In older cultures therefore there is a greater chance of isolating weak individuals, which then produce no colony.

Further, at the time of isolating unnecessarily long illuminations must be avoided. Since however in this method the light must be fairly strong, particularly in a power of 1000 times, it is best to work with artificial light, for instance with incandescent light from which the chemically active rays of ultra violet have been eliminated off. For this purpose the well known glass bulb is used; in this case it is not filled with ammoniacal copper oxide but with a not too dark solution of potassium dichromate (1 gram suffices for a globe of 3.5 litres). If one wishes somewhat to soften the yellow light, which according to some is harmful, to the eyes, this can be done by placing a thin cobalt blue glass on the iris-diaphragm.

Other important improvements are connected with the use of the moist chamber on which the coverslip is placed after the actual isolation has been accomplished.

On consulting the handbooks on the method of making the so-called drop-cultures in moist chambers, one gets in general the impression that such cultures must invariably succeed. For years I knew no better, and attributed the miscarriage of many of the cultures I made to faults in my method of work, until I found in KÜSTER's "Kultur der Mikroorganismen" on p. 54 the statement that all kinds of factors may here operate unfavourably. And when with reference to the papers quoted there, I read among others the broadly conceived and carefully executed experiments of CLARK and of DUGGAR[1], I saw that they had had the same experience as myself. CLARK comes to the conclusion that some micro-organisms are sensitive even to slight differences in the concentration of the culture-drop, or to the vapour pressure inside the moist chamber. On the floor of the latter he places no drops of water but some drops of the same fluid in which the culture is grown. Then the vapour-pressure of the culture-drop and of the drops on the floor will be the same, and therefore there can be no reason for the culture-drop taking up or giving off water vapour, by means of which the concentration is altered. Since the rise of temperature in the closed space of the moist chamber is also detrimental, CLARK did not at once wholly close it with the cover-slip on placing it in the incubator, but left a small slit, which was afterwards closed. Further CLARK used relatively large moist chambers, for instance, a glass cylinder of $17\frac{1}{2}$ mm. in external diameter and 10.7 mm. in height. Attention should be paid to these suggestions, as far as is possible, and also the cleaning of the cover-slip on which the investigators above-mentioned lay special stress is not to be

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[1] J. F. CLARK, On the toxic effect of deleterious agents on the germination and development of certain filamentous Fungi. Bot. Gazette 1899. vol. 28. p. 289. B. M. DUGGAR, Physiological studies with reference to the germination of certain fungus spores. Bot. Gazette. 1901. vol. 31 p. 38.

[2] l. c. p. 294.

considered as of secondary importance. The cover-slips must be fairly new, at any rate not so old as to show signs of weathering (microscopically to be recognised as small scratches, — an appearance also given, however, by some impurities). **Clark** and **Duggar** describe in detail their method of cleaning; I myself boil them about 10 min. in a soap-solution, then they are well rinsed in plenty of ordinary water, preferably separately, and are stored dry. Other methods of cleansing, such as in the well-known mixture of potassium dichromate or in aether, can of course precede, if necessary, this boiling in a soap-solution.

Only by using *good* cover-slips can sharply defined drops be obtained. Further the slips must a short time before isolation be smeared with vaseline; if this is done some days before, then the drops are not so good. The diluting of the material is an important factor. The best and simplest method I found to consist in placing a very large drop of fluid on an ordinary cover-slip which has been prepared with vaseline.

This can be done much better than with the eye of a needle, by using a strip of platinum foil ± 5 c.m. in length, ± $2^1/_2$ mm. in breadth, which is bent longitudinally at right angles into a small gutter and which is further treated as an ordinary inoculation needle. About this drop one need not be so particular, as it is a large one; some material is introduced into it, and there distributed. If too much has been introduced some may be removed by the gutter-needle and then liquid is again added. The material drops are taken out for the purpose of isolation, and it is preserved, when necessary, in a moist chamber.

In my last publication I stated that the material drops should always consist of physiological sodium chloride solution, because then the isolated droplet separates most readily from the large drop. In my later experiments I found that some other fluid may also be used for the purpose, although they are slightly less suitable; such are meat broth, glucose-peptone for yeast and moulds, etc.

Finally a few hints and improvements may be mentioned.

By capillarity particles of vaseline and bacteria may sometimes dry on the ends of the isolating needles, especially if they are not cleaned immediately after use. In this case mere dipping into sulphuric acid is not enough; it is best first to wash the ends with ether, then to keep them for a quarter of an hour in concentrated sulphuric acid heated to 100° on a water bath.

The slit in the isolated chamber, through which the needle projects, is closed with liquid paraffin, thickened with a little finely divided vaseline; this is preferable to thickened olive oil and diapalm, as previously indicated.

The coverslips are not fastened to the moist chambers by means of vaseline, but by a mixture of 20 volumes of vaseline with 1 volume of paraffin, which can resist a temperature of 37° without melting.

I should gladly have limited myself to the above as regards the technique of my method, had I not thought it necessary to add some remarks concerning a paper by Mr. A. W. NIEUWENHUIS, in the Proceedings of the meeting of Nov. 26 last, entitled: "Method for growing micro-organisms out of a single cell". I will not refer to the *principal* features of the method, as they are quite the same as those of my own. I only propose to consider the objections, which NIEUWENHUIS raises against my method, and the modifications which he has hence thought necessary to introduce into the more delicate manipulations.

NIEUWENHUIS applies four tests to an isolation method and says there is no method satisfying these tests. The first of these is that isolations can be carried out at magnifications of 300 and higher (N. uses magnifications of 300 and 350). My method of course complies with this test, for all my isolation experiments with bacteria were carried out with a $^1/_{16}$ oil immersion LEITZ, therefore at a magnification of about 1000.

The second test is that the organism to be isolated should not be harmed by either chemical or physical stimuli. As regards *chemical* stimuli, NIEUWENHUIS asserts, that when my eye-shaped needles have been desinfected with sulphuric acid and ammonia, substances remain behind which irritate the cells, and that I myself give the proof of this, on p. 113 of my dissertation. In reality however I pointed out there, that this is only the case if the sterilisation is not conducted *properly*, i.e. if the needles are placed more deeply in the sulphuric acid than in the ammonia, so that the superfluous acid ascends towards the point of the needle. I added explicitly: "When I again "isolated the bacterium, while avoiding these mistakes, its power of "liquefaction was found equally strong after the isolation. The absence "of growth of the colonies then caused no more trouble". That this sterilisation should have harmful consequences, I have never been able to discover, although I have specially investigated the question by making parallel experiments with sterilized and non-sterilized isolation needles. Moreover the needle is always washed before use in a sterile drop on the isolation coverslip, and beforehand the needle may be held for a moment in a tube with sterile water at 100°, in which any trace of ammonium sulphate, *should* it have remained behind, dissolves very rapidly. I do not however, believe that this salt ever remains behind, for one always finally dips into excess of ammonia, and this evaporates in a few seconds. No mention is further made of harmful *physical* stimuli; we can therefore leave them out of account. I will merely observe now that in *dragging* the isolated cell across as I did originally (see my dissertation) and as NIEUWENHUIS still does, there is a greater danger than in *carrying* it across according to my method (see below).

The third test which my method is not supposed to satisfy, is that of the greatest possible simplicity, so that the *modus operandi* is within the reach of every investigator. This seems indeed to be the gravest objection, for at the beginning of his paper NIEUWENHUIS disposes of my method as pretty well useless. "It is — so he says there much too complex for a general application, as it requires too much from the dexterity and patience of the investigator on account of the long time too, wanted in the application it would be troublesome even for a skilful experimentor, frequently to use it". As regards this point, I cannot do better than quote my conclusion in my last paper [1]: durch einige Uebung bringt man es bald so weit, dass, wenn das Material ungefähr die richtige Verdünning hat . . . . man in ungefähr 5 Minuten eine Bakterie aus den Materialtropfen isoliert und in den Kulturtropfen bringt". And this applies to *bacteria*; fungus spores and yeast cells are treated still more easily. Experience has moreover taught me that anyone who is quite new to the method, acquires it as rapidly as the methods for staining spores or cilia.

The fourth test, that asepsis should be easily maintained, is not further advanced as an objection to my method. Perhaps NIEUWENHUIS is thinking here of my moist chambers which I do not pass through a flame each time, but which are internally coated with vaseline. In the hundreds of experiments which have gone through my hands, I have never observed a single case of infection; the vaseline retains the organisms which fall on it, and the latter do not germinate.

With reference to the above demand for simplicity, it might be pointed out that there is yet another objection to my method: the difficulty of making the glass needles. Certainly NIEUWENHUIS' needles are made more easily. In my last paper I mentioned however, on p. 18, that, so long as the method of manufacture had not yet been published, I would gladly personally help any one, who desired it. I wrote: "Eventuelle Anfragen werde ich indessen vorläufig gern entgegennehmen". And this I have always done disinterestedly —

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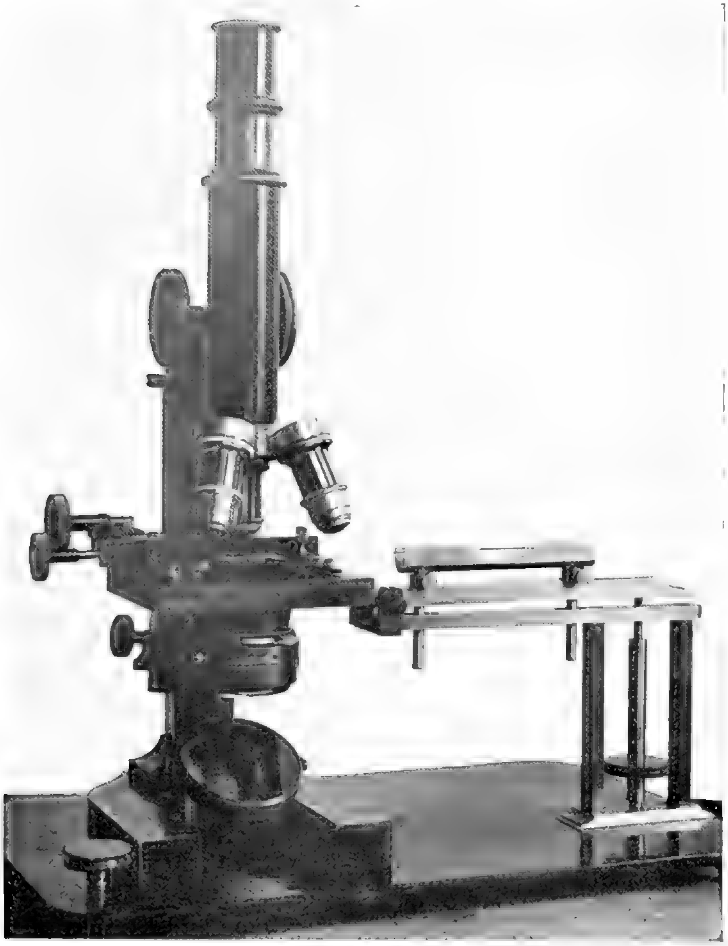
[1] p. 26.

S. L. SCHOUTEN. "Pure cultures from a single cell, isolated under the microscope."



Apparatus for isolating a single cell.

when my own countrymen were concerned — also for instance when Mr. **Nieuwenhuis** began to work with my method. Moreover I have published the method of making the needles, and have pointed out that any one can easily make the simple mechanism required [1]).

Meanwhile I emphasise, that this has nothing to do with the *modus operandi* of the method. One can hardly for instance call the *modus operandi* of telephoning complicated, because the manufacture of the telephone mechanism is difficult.

So much as regards the objections to my method, of which I appreciate the last one — the difficulty of making the glass needles and the fact that they could not be obtained commercially; I am therefore all the more glad that this objection has been removed.

I now wish to discuss the alterations introduced by **Nieuwenhuis** in my method.

Fearing the above mentioned imaginary danger in sterilising the isolation needles, **Nieuwenhuis** has preferred to make for each isolation a new needle which terminates in a globule instead of an eye and which must be fastened into the needle-holder by means of plaster of Paris. It seems unnecessary to show that this is much more cumbrous than working continually with the same needle, which, when necessary, is readily sterilized in the way described. One can work for years with a single needle; it is elastic and does not break unless it is knocked roughly or dropped.

Nieuwenhuis has the needle fixed to a support stand, which stands separately next to the microscope, while in my apparatus the support and microscope stand on the same plate, so that a displacement of the support with respect to the microscope, for instance through a knock, is rendered impossible. In the support used by **Nieuwenhuis**, the needle can be moved in 3 directions, which is quite superfluous if a mechanical stage is used, as I have done from the beginning. Meanwhile **Nieuwenhuis** (p. 533) eventually came to the same conclusion. He further places the coverslip, in which the cell is to be isolated, under the microscope in a kind of chamber, which is quite open on one side in order to admit the isolation needle. In my apparatus the needle enters through a slit, which is closed with liquid paraffin. By this means a closed moist chamber is formed, which has the great advantage, that if a drop is placed on its floor, even the smallest isolated droplet does not evaporate, so that observations can be made on isolated cells for a whole day,

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[1]) Zeitschr. für wiss. Mikr. Technik Bnd. 24, 1907, p. 258. **Burry** — in his "Tuscheverfahren" wrongly assumes that the price of this simple mechanism is 100 Mk, which is the price of the apparatus for *isolation*.

if necessary. That asepsis is better secured by this arrangement than by the chamber of NIEUWENHUIS, which is 8 m.m. high and quite open on one side, requires no further proof.

My principal objection is, however, to the circumstance, that NIEUWENHUIS drags the isolated cell in the droplet over the glass to the culture drop. This he cannot avoid, as he uses a club shaped needle.

In my dissertation I also transferred the cells by dragging, but, with a few exceptions, I have departed from this in later years. One of the reasons, which certainly may be advanced, is that this dragging, in the case of very small cells, fatigues the eye. The principal reason, however, is that the cells remain behind, especially in the case of long thin rodlike bacteria, spirillae, and spirochaetes. There are all sorts of cells which it is not possible to drag across, even in a large transport drop; such a drop has further the disadvantage that a contaminating bacterium is not readily discovered in it. NIEUWENHUIS states, that with him even spores sometimes adhere to the lower surface of the coverslip. No wonder, especially if one further considers that the isolated droplet begins to evaporate in its journey across the chamber, which is open on one side. If a cell remains behind, he advises placing the knob behind it and then moving it on; he admits however that thus the danger of injury arises. It is evident that micro-organisms with long fine cilia are not improved by dragging along, and that one may safely call this a harmful physical stimulus. On account of all these reasons I use an eyelet in which I take up one cell, and place it at once without dragging it, next to the culture drop. Only in very few exceptional cases, as for instance when the cell for some reason or another could not be easily taken up in the eyelet, one can have recourse to this dragging (for which my eye-shaped needle can also be used), but with my method at least the transport-drop will not evaporate while on the way. I can as little welcome the modification of bringing the cell at once into the culture-drop with the same needle with which it was isolated.

NIEUWENHUIS says on p. 532: "it is clear that the parts to be transferred must be as far as possible from one another in the drop of the material, in order to avoid a contamination of the needle; from this it follows that the material must be very dilute".

I willingly grant that when the cells occur far from one another in the drop, one can be fairly sure that on taking the cell out of the drop the needle will not be contaminated by the neighbouring cells. When, however, in a mixture only comparatively few cells of a certain kind occur, and one just requires that particular kind, it ought not to be so much diluted, because the chance of getting cells at the edge is much too small. And then there is certainly the risk that in isolating one cell, one brings with it other cells which cause the experiment to fail. Therefore I still find the use of two needles necessary for *difficult* cases (also, for instance, in dealing with mucilaginous material). With the first needle the cell isolated is brought near to the culture-drop, with the second, which is then certainly still sterile, it is put into it.

In my original apparatus the needles are always placed on either side of the microscope, on two separate stands; in my simplified arrangement with one needle stand, the first needle is in such cases replaced by the second. For this naturally the cover slip used for isolating must momentarily be placed on an ordinary moist chamber. One can however, without the microscope, also stretch the culture-drop with an ordinary platinum inoculation needle somewhat near to the edge of the isolated droplet; then also the isolated cell will come into it.

There are still a few short remarks.

Before Nieuwenhuis lays the cover-slip, on which the isolation has taken place, on the moist chamber for the further development of the culture, he absorbs the drop of the material by means of a filter paper. With his method this is necessary, for the drops must for the purpose of being dragged lie close to another and this is very likely to give rise to contamination of the culture-drop by hyphae which grow out of the drop of the material.

Whilst it remains doubtful whether after this absorption no cells are left behind, and germinate in the moist chamber, I here point out that by my method the distance can be so great that there can be no question of any such infection. I have never had any trouble from it. There are advantages in leaving the drop of material in its original place. The behaviour of the cells occurring in it (whether the spores develop, whether the bacteria remain mobile) sometimes enables important conclusions to be drawn.

Nieuwenhuis lays no drop on the floor of the moist chamber, because then the too considerable condensation on the cover slip is troublesome.

This difficulty is avoided if the slips are cleaned in the way described above, and if the moist chamber is not — as in his method — placed on a fixed object in the incubator, so that the slide is the warmest, but is, for instance, placed in a small box on 2 strips of wood. Nieuwenhuis thinks that the slight evaporation from a large culture-drop can have no harmful consequences; after the above mentioned investigations of Clark and Duggar caution is however advisable.

Taking everything into consideration among the changes which Nieuwenhuis proposes in my method, there is only one with which (and then only partly) I am in agreement and which is also incorporated in my simplified apparatus (of which I had wished, for certain reasons, to postpone the publication): the two needle holders are replaced by one. When however he advises always the use of not more than one needle in isolating, we differ entirely. If he had carried out more extensive investigations with difficult material, for instance, with bacteria, instead of with the much larger fungus spores, he would not have suggested any alteration.

I should be glad if the fact that the needles can now be obtained commercially, should lead to a more extensive use of my method. I am convinced that it has a large sphere of usefulness. Those who from the detailed description in my last publication conclude that the method is too difficult, are mistaken: I have thought it preferable to go into a minute description in order to make it as easy as possible for those who use it, however tempting it was to give the impression of a too great simplicity by a cursory description.

For the rest, those who hesitate to isolate bacteria, can work with yeast or moulds.

The technique of the method will improve by extensive use, for I cannot imagine it to be perfect.

With regard to the alterations, proposed by Nieuwenhuis, I felt obliged to say at once, that in my opinion, they are not improvements.

Finally one hint more: I advise those who can afford it to procure the apparatus with a moveable stand, on which the microscope is placed; although it seems to be more complicated it is the more convenient in use.

Mathematics. — *"On the integrating of series term-by-term".* Communicated by Mr. J. C. Kluyver.

(Communicated in the meeting of January 28, 1911).

When the function $F(x)$ is developed in a series converging uniformly for $a \leq x \leq b$, we can integrate term-by-term, i.e., out of the equation

$$F(x) = \sum_{0}^{\infty} u_n(x)$$

follows

$$\int_a^b F(x)\,dx = \sum_0^\infty \int_a^b u_n(x)\,dx.$$

We may not conclude to this last equation as soon as one of the two limits of the domain of integration is just excluded from the interval of the uniform convergence.

Wellknown instances have shown, that in that case the rule of the integration term-by-term may hold or not.

Instances. The series $\sum_0^\infty u_n(x)$ converges uniformly for $0 \leqq x < 1$.

I. $\sum_0^\infty u_n(x)$ converges for $x = 1$.

$u_n(x) = (n+1)(1-x)x^n - (n+2)(1-x)x^{n+1}$.

$$F(x) = (1-x) \quad , \quad \int_0^1 F(x)\,dx = \frac{1}{2} \quad , \quad \sum_0^\infty \int_0^1 u_n(x)\,dx = \frac{1}{2}\,.$$

$u_n(x) = n(1-x)\,e^{-n(1-x)^2} - (n+1)(1-x)\,e^{-(n+1)(1-x)^2}$.

$$F(x) = 0 \quad , \quad \int_0^1 F(x)\,dx = 0 \quad , \quad \sum_0^\infty \int_0^1 u_n(x)\,dx = -\frac{1}{2}\,.$$

$$u_n(x) = \frac{(1-x)\,n^{\frac{3}{2}}}{1+(1-x)^4 n^2} - \frac{(1-x)\,(n+1)^{\frac{3}{2}}}{1+(1-x)^4 (n+1)^2}\,.$$

$$F(x) = 0, \quad \int_0^1 F(x)\,dx = 0 \quad , \quad \sum_0^\infty \int_0^1 u^n(x)\,dx \text{ diverges.}$$

II. $\sum_0^\infty u_n(x)$ diverges for $x = 1$.

$u_n(x) = (-1)^n x^n$.

$$F(x) = \frac{1}{1+x} \quad , \quad \int_0^1 F(x)\,dx = log\,2 \quad , \quad \sum_0^\infty \int_0^1 u_n(x)\,dx = log\,2.$$

$u_n(x) = (n+1)\,x^n - (n+2)\,x^{n+1}$.

$$F(x) = 1 \quad , \quad \int_0^1 F(x)\,dx = 1 \quad , \quad \sum_0^\infty \int_0^1 u_n(x)\,dx = 0.$$

$u_n(x) = (-1)^n (n+1)\,x^n$.

$$F(x) = \frac{1}{(1+x)^2} \quad , \quad \int_0^1 F(x)\,dx = \frac{1}{2} \quad , \quad \sum_0^\infty \int_0^1 u_n(x)\,dx \text{ diverges.}$$

When the upper limit b of the range of integration belongs no more to the interval of the uniform convergence, we can prove still pretty simply in some suppositions, that the integrating term-by-term gives a correct result.

We are sure of this, when the series $\sum\limits_0^\infty u_n(x)$ converges uniformly for $a < x < b$, when the series of integrals converges absolutely and when moreover each term $u_n(x)$ has a constant sign in the whole domain of integration.

For, now we find in the first place for $a \leq t < b$

$$\int\limits_a^t F(x)\,dx = \sum_0^\infty \int\limits_a^t u_n(x)\,dx.$$

Of this last series the absolute value of each term is smaller than the corresponding term of the convergent series

$$\sum_0^\infty \left| \int\limits_a^b u_n(x)\,dx \right|,$$

from which ensues that with respect to t the series

$$\sum_0^\infty \int\limits_a^t u_n(x)\,dx$$

converges uniformly in the domain $a \leq t \leq b$.

The principal property of the uniformly convergent series furnishes then immediately

$$\int\limits_a^b F(x)\,dx = \underset{t=b}{Lim} \sum_0^\infty \int\limits_a^t u_n(x)\,dx = \sum_0^\infty \int\limits_a^b u_n(x)\,dx.$$

Very often this theorem proves sufficient. Thus we find that for $0 < x < 1$ the equation holds:

$$F(x) = \frac{\left(\log \frac{1}{x}\right)^{s-1}}{1+x} = \sum_0^\infty (-1)^n \left(\log \frac{1}{x}\right)^{s-1} x^n,$$

and the development at the right-hand side is in this interval uniformly convergent.

The series of the integrals

$$\Gamma(s) \sum_1^\infty \frac{(-1)^{n-1}}{n^s}$$

converges absolutely, if only $s > 1$ and under this condition therefore the equation

$$\int_0^1 \frac{\left(log\frac{1}{x}\right)^{s-1}}{1+x}\,dx = \int_0^\infty \frac{y^{s-1}}{e^y+1}\,dy = \Gamma(s)\sum_1^\infty \frac{(-1)^{n-1}}{n^s}$$

will hold.

However the theorem under discussion does not serve to show that the above equation remains correct for $0 < s \leq 1$. Here as well as in other cases this theorem needs amplifying and as such the following theorem can sometimes serve.

When $F(x)$ is developed in a series of continuous functions we shall be able to deduce

$$\int_a^b F(x)\,dx = \sum_0^\infty \int_a^b u_n(x)\,dx,$$

out of

$$F(x) = \sum_0^\infty u_n(x)$$

as soon as is given:

1st. $\sum_0^\infty u_n(x)$ is convergent for $a \leqq x < b$.

2nd. $\sum_0^\infty \int_a^b u_n(x)\,dx$ converges.

3rd. The function $u_n(x)$ does not change its sign in the interval $a < x < b$.

4th. $\left|\frac{u_{n+1}(x)}{u_n(x)}\right|$ is monotonic with respect to x and that for all values of the index n in the same sense.

In order to prove this theorem we must show in the first place, that the series to be integrated converges uniformly for $a \leqq x < b$. In the main this follows out of the fourth datum, which states that for all values of n the inequality

$$\left|\frac{u_{n+1}(x)}{u_n(x)}\right| \leqq \left|\frac{u_{n+1}(y)}{u_n(y)}\right|$$

will exist when $x < y$, or that for all values of n that inequality will hold when $x > y$.

I first suppose that the inequality holds for $x < y$. On the ground of the third datum we find

$$\alpha_n = \frac{u_n(x)}{u_n(y)} \text{ and } \alpha_{n+1} = \frac{u_{n+1}(x)}{u_{n+1}(y)}$$

to be positive numbers and the inequality expresses that $\alpha_{n+1} \leqq \alpha_n$.

In the sequence

$$\alpha_p, \quad \alpha_{p+1}, \quad \alpha_{p+2}, \ldots$$

the numbers are therefore not ascending and as according to the first datum the series $\sum\limits_0^\infty u_n(y)$ converges, we conclude from the well-known lemma of ABEL, that

$$\sum_p^\infty u_n(y)\alpha_n = \sum_p^\infty u_n(x)$$

is situated between $G\alpha_p$, and $K\alpha_p$, where G and K denote successively the upper limit and the lower one of the sums:

$$u_p(y), \quad u_p(y) + u_{p+1}(y), \quad \ldots, \quad u_p(y) + u_{p+1}(y) + u_{p+2}(y) + \ldots$$

If we take p large enough $|G|$ and $|K|$ remain below an arbitrary small quantity ε, so that we have for p large enough:

$$\left|\sum_p^\infty u_n(x)\right| < \varepsilon\alpha_p.$$

In the supposition under discussion here concerning the fourth datum follows out of the convergence of $\sum\limits_0^\infty u_n(y)$ the uniform convergence of the series $\sum\limits_0^\infty u_n(x)$ for all x, satisfying $a \leq x < y$, and as we can make y tend to b, the uniform convergence for $a \leq x < b$ has been proved.

In the same way we might have concluded out of

$$\left|\frac{u_{n+1}(x)}{u_n(x)}\right| \leq \left|\frac{u_{n+1}(y)}{u_n(y)}\right|$$
$$(x > y)$$

the uniform convergence of $\sum\limits_0^\infty u_n(x)$ in the range $y < x \leq b$, and as this series converges for $x = a$, we should have uniform convergence in the whole interval of integration $a \leq x \leq b$, from which would immediately follow what is to be proved. So we have only to investigate further the supposition

$$\left|\frac{u_{n+1}(x)}{u_n(x)}\right| \leq \left|\frac{u_{n+1}(y)}{u_n(y)}\right|,$$
$$(x < y)$$

where the series converges uniformly in the domain $a \leq x < b$ and where divergence for $x = b$ remains possible.

When we put

$$\beta_n = \frac{\int\limits_a^t u_n(x)dx}{\int\limits_a^b u_n(y)dy}.$$

then this number, because $u_n(x)$ has a definite sign in the range of integration $u_n(x)$, is positive and smaller than unity.

The numbers

$$\beta_p , \quad \beta_{p+1} , \quad \beta_{p+2} \ldots$$

are not ascending, for we have

$$\beta_n - \beta_{n+1} = \frac{\int\limits_a^t u_n(x)\, dx}{\int\limits_a^b u_n(y)\, dy} - \frac{\int\limits_a^t u_{n+1}(x)\, dx}{\int\limits_a^b u_{n+1}(y)\, dy},$$

or

$$\beta_n - \beta_{n+1} = \frac{\int\limits_a^t dx \int\limits_t^b dy \; u_n(x) \; u_n(y) \left\{ \frac{u_{n+1}(y)}{u_n(y)} - \frac{u_{n+1}(x)}{u_n(x)} \right\}}{\int\limits_a^b u_n(y)\, dy \, . \int\limits_a^b u_{n+1}(y)\, dy},$$

and as in the double integral y always remains larger than x, the double integral can in connection with the supposition just made concerning the fourth datum never be negative.

Again we can apply the lemma of ABEL, from which ensues that

$$\sum_p^\infty \beta_n \int\limits_a^b u_n(y)dy = \sum_p^\infty \int\limits_a^t u_n(x)dx$$

is lying between $\beta_p G'$ and $\beta_p K'$, where G' and K' denote successively the upper and lower limit of the sums

$$\int\limits_a^b u_p(y)dy, \quad \int\limits_a^b u_p(y)dy \quad \int\limits_a^b u_{p+1}(y)dy, \; \ldots\ldots$$

$$\int\limits_a^b u_p(y)dy + \int\limits_a^b u_{p+1}(y)dy + \int\limits_a^b u_{p+2}(y)dy + \ldots\ldots$$

By taking p large enough we can make $|G'|$ and $|K'|$ according to the second datum smaller than an arbitrary small quantity ε and for p large enough we have thus at the same time

$$\left| \sum_p^\infty \int_a^b u^n(y)dy \right| < \varepsilon,$$

$$\sum_p^\infty \int_a^t u_n(x)dx \,\Big| < \beta_p\, \varepsilon < \varepsilon.$$

By these inequalities is expressed that the series

$$\sum_0^\infty \int_a^t u_n(x)dx$$

converges with respect to t uniformly in the domain $a \leq t \leq b$. We have already proved that in the domain $a \leq x < b$ the series $\sum\limits_0^\infty u_n(x)$ converges uniformly, so that the equation

$$\int_a^t F(x)dx = \sum_0^\infty \int_a^t u_n(x)dx$$

certainly holds, and when we then finally apply the principal property of the uniformly convergent series we find when t tends to b

$$\int_a^b F(x)dx = \mathop{Lim}_{t=b} \sum_0^\infty \int_a^t u_n(x)dx = \sum_0^\infty \int_a^b u_n(x)dx.$$

With this we have given the proof of the enunciated theorem and it is clear that the proof holds if the third and fourth data only hold for all numbers n surpassing a definite number.

For the evaluation of the integral

$$\int_0^\infty \frac{y^{s-1}}{e^y+1} = \int_0^1 \frac{\left(log\, \frac{1}{x}\right)^{s-1}}{1+x}\, dx$$

(where $s > 0$) the theorem can be applied.

We have

$$\frac{\left(log\, \frac{1}{x}\right)^{s-1}}{1+x} - \left(log\, \frac{1}{x}\right)^{s-1} = \sum_1^\infty (-1)^n \left(log\, \frac{1}{x}\right)^{s-1} x^n,$$

and the series converges for $0 < x < 1$. The terms do not change signs for $0 < x < 1$, the quotient

$$\frac{u_{n+1}(x)}{u_n(x)} = x$$

increases with x. The series of the integrals

$$\Gamma(s) \sum_{2}^{\infty} \frac{(-1)^{n-1}}{n^s}$$

converges for $s > 0$. The theorem therefore holds and we find for all positive values of s

$$\int_0^\infty \frac{y^{s-1}}{e^y+1}\, dy = \Gamma(s) \sum_{1}^{\infty} \frac{(-1)^{n-1}}{n^s}.$$

In general we shall often be able to use this theorem when evaluating an integral of the form

$$\int_0^1 f(x)\, g(x)\, dx.$$

Suppose it possible to replace $f(x)$ by a power series $\sum\limits_0^\infty a_n x^n$ such that the series $\sum\limits_0^\infty a_n x^n g(x)$ diverges for $x = 1$, but that the series of the integrals

$$\sum_0^\infty a_n \int_0^1 x^n\, g(x)\, dx$$

is still convergent. Then this series will certainly be equal to the integral, if only $g(x)$ does not change its sign in the domain of integration, because then all conditions under which the theorem holds are satisfied.

We shall likewise, if the development

$$f(x) = \sum_0^\infty a_n x^n$$

holds for all finite values of x, be allowed to conclude by means of the theorem to the equation

$$\int_0^\infty f(x) e^{-x}\, dx = \sum_0^\infty n!\, a_n,$$

if this last development converges.

Physics. - *"Some remarks on the mechanical foundation of thermodynamics."* [1]) II. By Dr. L. S. ORNSTEIN. (Communicated by Prof. H. A. LORENTZ.

(Communicated in the meeting of Januari 28, 1911).

§ 4. In § 2 I have discussed some ensembles and I have shown that they can be used to deduce the properties of a real system because they are connected with the time ensemble and because the majority of their systems is equivalent. I shall give in this paragraph another deduction which for this purpose may show the importance of the energy-space ensemble (and of the microcanonical one).

If in reality we want to obtain a system with a given energy we take a system of the same kind and supply energy to it or abduce energy from it, giving at the same time the appropriate values to the external coordinates. Let us suppose that it is possible for us to construct a system that contains exactly the required energy. If we do not take special care to get a system of a definite internal state, we shall obtain by our operations one of the systems possible with the given energy, but it will be impossible to indicate what kind of system will be produced. We can by no means practically regulate the internal state arbitrarily, as it is impossible for us to influence directly a single degree of freedom (e.g. the phase of the molecules). But we can only give the values we desire to the energy, density, or concentration in rather large parts, and even this with a moderate precision. If in a great number of cases we give the energy ε to a system we shall obtain it over and over again in other states, and the same will be the case if we bring the energy of a great number of systems together to the value ε.[2]) The ensemble obtained in this way may be called a "real" energy space-ensemble.

Instead of giving the energy ε to N systems we can also select them in nature. I shall term the ensemble thus obtained a nature energy-space ensemble. The real and the nature energy-space ensemble

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[1]) See These Proceedings page 817. Putting for the probability of the homogeneous system w_0 we find for that of a system specified by the numbers τ_l

$$w = w_0 \, e^{-\frac{n}{k} \sum_{1}^{k} \tau_l^2 \beta}$$

β is a function of the volume, the diameter of the molecules and the temperature.

[2]) The circumstance must be taken into account that the original system will differ also in phase.

are not identical; the following considerations mutatis mutandis may, however, be applied to both. I shall therefore in the following pages only take into account the real energy-space ensemble. Constructing several times a real energy space ensemble, we shall find that the number of systems lying in a given element of the space E_{2n-1}, can differ in those cases. How great this number will be, cannot be said, if one does not know anything about the way in which the energy is supplied to the systems. If, however, we proceed without any scheme, the distribution of systems over the space E_{2n-1} will differ very little in the majority of possible cases. The distribution occurring in the majority of the possible cases must be stationary. The most simple stationary ensemble is the energy space ensemble discussed in § 2.[1]).

I shall now introduce the hypothesis that the real ensemble is identical with an energy space ensemble.

If we had supposed the energy of the considered systems to have a value between ε and $\varepsilon + d\varepsilon$, we should have found another kind of real ensembles which we can indicate by the term of real microcanonical ensembles. The most frequently occurring and stationary ensemble is the ensemble with a homogeneous distribution. (Comp. GIBBS Chap. XI and XII).[1])

The introduced hypothesis enables us to deduce the properties of a real system with the help of the corresponding mean value in the energy space or the microcanonical ensemble. An arbitrary system can be obtained by choosing a system from a real ensemble; this real ensemble is an energy-space or microcanonical ensemble; the

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[1]) The ensembles having the constant A different for the strips are also stationary. These must be taken into account if we know something more concerning the constants of integration.

[2]) The distribution of systems in a real ensemble can be changed by the motion of the representing points, if it is not identical with the energy space-ensemble. It is impossible that in consequence of this motion an arbitrary real ensemble changes to an energy space ensemble, if the distribution for the strips of § 3 deviates from that in the energy space ensemble. Suchlike ensembles are, however, very rare among all the ensembles, built up of a given number of systems in the space E_{2n-1}. If the distribution over the strips agrees with that in an energy space ensemble, but is different from this inside the strips themselves, the ensemble will, by the motion of the systems, take states in which it deviates very little from an energy space ensemble but periodically it will again differ more from it. Also this kind of deviating ensembles is very rare. As for a real microcanonical ensemble, which shows a distribution different from the homogeneous, the distribution will differ after a long time as little as we like from the homogeneous in fixed elements of the space E_{2n-1} which are not too small. (Comp. GIBBS Chap. XII.)

properties of a real system are therefore those of a system chosen arbitrarily from one of those ensembles.

If we know that the state of a system is stationary, the properties of the system will agree with those of the most frequently occurring system of the ensemble; after a sufficiently long time every system will come to this state just for the very reason one would say that it can be thought to belong to a real ensemble. The idea of probability of a real system, which strictly speaking has only sense in relation to systems lying on the same path, can now be extended in the following manner: the system is produced by a construction which when repeated many times will lead to a real ensemble, the latter is identified with an energy-space (or microcanonical) ensemble; the probability that a real system is in a given state is therefore equal to the probability of the same state in the energy space or microcanonical ensemble [1]).

§ 5. In the following I shall consider the canonical ensembles. It is generally affirmed that these ensembles have no physical meaning and that their introduction is only justified because of the simplifications, which they allow when used in the calculations; also **Hertz** adheres to this opinion [2]). I think, however, that by changing a little the considerations which enabled us to ascribe a physical meaning to the microcanonical ensemble, i. e. by relating them to the real ensembles, we can attribute *in the same sense* a physical meaning to the canonical ensembles. If we know that in nature by the action of exactly determined causes a system of precisely the energy ε_0 would be formed, it is obvious to presume that in consequence of the small

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[1]) By the following considerations we can avoid the mentioned hypothesis. Suppose that a real ensemble has been constructed $\mathfrak{N}$ times; in each construction we take N times a point at haphazard in the space E_{2n-1} and unite the chosen points to an ensemble (or we proceed in the same way for the layer between ε and $\varepsilon + d\varepsilon$). Each possible real ensemble appears a certain number of times among the $\mathfrak{N}$ ensembles constructed. The probability W_ν of a given ensemble can be defined, as this number divided by the total number of ensembles $\mathfrak{N}$. If w_ν represents the probability of a given state in the ensemble under consideration then $\sum_1^{\mathfrak{N}} w_\nu W_\nu$ can be taken as the definition of the probability of a phase, the sum has to be extended over all the $\mathfrak{N}$ ensembles. The hypotheses mentioned above means that we put the probability for the energy-space ensemble equal to 1 and take for w the probability in their ensemble.

[2]) This simplification is often not so very important; most questions which can be solved by means of the canonical ensembles can be treated in a like manner without much complication, also by means of the micro-canonical ensembles.

and accidental deviations in the several causes not a system of exactly the energy ε_0 will be produced, but one of the energy ε; in general $(\varepsilon_0 - \varepsilon)$ will be small in comparison to ε_0. Positive as well as negative deviations will occur.

If we now construct a real system by trying to give the energy ε_0 to N systems or by choosing N systems of this kind in nature, we shall suppose that the probability that a system of the energy $\varepsilon_0 + \varepsilon'$ will be chosen is as great as that for the one with the energy $\varepsilon_0 - \varepsilon'$; a hypothesis which will be plausible as long as ε' is small. If the hypothesis is right, it may easily be shown that the canonical ensemble will play a part in the definition of the probability of a system.

In analogy of other cases (e. g. the law of errors) it seems admissible to suppose that in a real ensemble the number of systems whose energy lays between ε and $\varepsilon + d\varepsilon$ can be represented by

$$NA\, e^{-(\varepsilon - \varepsilon_0)^2 k}\, d\varepsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

It is not possible to prove this formula as long as we know nothing about the way in which the energy is supplied to the systems, or in which the energy ε_0 of the systems chosen from nature is determined [1]).

If we form hypotheses on this subject we can deduce (15), but much importance should not be ascribed to such a deduction. [2])

Proceeding further in the same way as in the case of the microcanonical ensembles we find for systems in the real ensemble which are represented in each layer between ε and $\varepsilon + d\varepsilon$ a homogeneous distribution.

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[1]) If we suppose that the ensemble is constructed by choosing the systems from nature, the measurement of energy will be subjected to an error, the analogy with the law of errors therefore is still more obvious. Only we have now the difficulty that we do not know in what distribution the different systems of a certain energy appear in nature.

[2]) To give an example take the following case. From a recipient of infinite energy, the energy is supplied to N systems. Equal portions α are supplied to a total amount of Nn portions to the systems of an initial energy 0. The supply of energy takes place in Nn distributions. In every distribution one system is taken from the N systems, the energy α supplied to it, and the system replaced among the others. This is Nn times repeated. It is evident that in a definite case not each system has obtained the energy $n\alpha = \varepsilon_0$, but it is possible to indicate the number of the systems containing an energy between $n'\alpha$ and $(n'-1)\alpha$. If the mentioned process is repeated several times, one distribution will be the most probable or most (frequently occurring) among all the possible distributions and this will be that for which (15) expresses the number of systems obtaining an energy between ε and $\varepsilon + d\varepsilon$. If α is infinitely small, we can be sure that the real ensemble obtained will be the ensemble characterised by (15).

If we represent the volume of the layer between $E_{2n-1}(\varepsilon)$ and $E_{2n-1}(\varepsilon + d\varepsilon)$ by $e^{\varphi(\varepsilon)}\, d\varepsilon$, $\varphi(\varepsilon)$ being a determined function of ε and we imagine an ensemble in which the density in the mentioned layer amounts to $f(\varepsilon)$, this ensemble will be identical with the real ensemble if

$$\frac{f(\varepsilon)\, e^{\varphi(\varepsilon)}}{f(\varepsilon_0)\, e^{\varphi(\varepsilon_0)}} = e^{-k(\varepsilon-\varepsilon_0)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

From (16) results

$$\log f(\varepsilon) - \log f(\varepsilon_0) + \varphi(\varepsilon) - \varphi(\varepsilon_0) = -k(\varepsilon-\varepsilon_0)^2$$

developing for small values of $(\varepsilon - \varepsilon_0)$ we get

$$(\varepsilon-\varepsilon_0)\left\{\left(\frac{d \log f(\varepsilon)}{d\varepsilon}\right)_{\varepsilon=\varepsilon_0} + \left(\frac{d\varphi(\varepsilon)}{d\varepsilon}\right)_{\varepsilon=\varepsilon_0}\right\} +$$

$$+ \tfrac{1}{2}(\varepsilon-\varepsilon_0)^2\left\{\left(\frac{d^2 \log f(\varepsilon)}{d\varepsilon^2}\right)_{\varepsilon=\varepsilon_0} + \left(\frac{d^2\varphi(\varepsilon)}{d\varepsilon^2}\right)_{\varepsilon=\varepsilon_0}\right\} = -k(\varepsilon-\varepsilon_0)^2.$$

Therefore

$$\left(\frac{d \log f(\varepsilon)}{d\varepsilon}\right)_{\varepsilon=\varepsilon_0} = -\left(\frac{d\varphi(\varepsilon)}{d\varepsilon}\right)_{\varepsilon=\varepsilon_0}$$

and

$$\left(\frac{d^2 \log f(\varepsilon)}{d\varepsilon^2}\right)_{\varepsilon=\varepsilon_0} = -\left(\frac{d^2\varphi(\varepsilon)}{d\varepsilon^2}\right)_{\varepsilon=\varepsilon_0} - 2k.$$

In first approximation

$$f(\varepsilon) = f(\varepsilon_0)\, e^{-\left(\frac{d\varphi(\varepsilon)}{d\varepsilon}\right)_{\varepsilon=\varepsilon_0}(\varepsilon-\varepsilon_0)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17),$$

If we suppose that this formula is true for all values of ε and that therefore $\frac{d^2 \log f(\varepsilon)}{d\varepsilon^2}$ can be put 0, we find for the number of systems having the energy between ε and $\varepsilon + d\varepsilon$

$$f(\varepsilon_0)\, e^{\left(\frac{d\varphi(\varepsilon)}{d\varepsilon}\right)_{\varepsilon=\varepsilon_0}\varepsilon_0 - \left(\frac{d\varphi(\varepsilon)}{d\varepsilon}\right)_{\varepsilon=\varepsilon_0}\varepsilon + \varphi(\varepsilon)}\, d\varepsilon\, .$$

Putting $\left(\frac{d\varphi(\varepsilon)}{d\varepsilon}\right)_{\varepsilon=\varepsilon_0} = \frac{1}{\Theta}$ and $f(\varepsilon_0)\, e^{\left(\frac{d\varphi(\varepsilon)}{d\varepsilon}\right)_{\varepsilon=\varepsilon_0}\varepsilon_0} = Ne^{\frac{\Psi}{\Theta}}$ we find for this number.

$$Ne^{\frac{\Psi-\varepsilon}{\Theta}+\varphi(\varepsilon)}\, d\varepsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

so the ensemble is canonical. The relation to be adopted between k and

$\left(\frac{d^2 \varphi(\varepsilon)}{d\varepsilon^2}\right)_{\varepsilon=\varepsilon_0}$ does not follow as far as I can see from the physical signification of these quantities [1]).

Gibbs has proved that the quantity $\left(\frac{\partial \varphi(\varepsilon)}{\partial\varepsilon}\right)^{-1}_{\varepsilon=\varepsilon_0}$ has properties corresponding with those of temperature. The mentioned quantity, however, has a definite value for a given value of the energy ε_0, so the modulus of the canonical ensemble used has to be put equal to the value of $\left(\frac{\partial \varphi}{\partial\varepsilon}\right)^{-1}_{\varepsilon=\varepsilon_0}$. The ensemble defined by (15) and the canonical ensemble (18) deviate slightly from each other, but these deviations are of less significance the greater the number of degrees of freedom is. The deviations are most important for those systems of which the energy ε is such that $(\varepsilon - \varepsilon_0)$ is large in comparison to ε_0, but suchlike systems are very infrequent in both ensembles. We can without fearing errors in our results suppose the real ensemble to be a canonical one, and if we further suppose that in the real ensemble the distribution in every layer is homogeneous, we find for the probability of a system in the real ensemble

$$e^{\frac{\Psi-\varepsilon}{\Theta}}\, dp_1 \ldots dq_n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (19)$$

The identity of the real and the canonical ensemble is no more fully proved or to be proved completely than that of the microcanonical or energy-space ensemble. It exists in this respect that the number of systems in the layer $\varepsilon \ldots \varepsilon + d\varepsilon$ can be represented by $f(\varepsilon)d\varepsilon$, $f(\varepsilon)$ being a maximum for $\varepsilon = \varepsilon_0$, as well for the real as for the canonical ensembles; in the microcanonical ensembles without it $f(\varepsilon) = 0$, to a certain degree the latter ensembles have therefore less physical sense than the canonical, provided that we do not take as startingpoint the single system and with it the time-ensemble, but take into account that a given system has a not totally definite energy.

§ 6. **Hertz** has developed in the paper mentioned considerations about the theorem that two systems of equal temperature produce

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[1]) Gibbs has proved (Chap IX (350)) that we have the relation

$$\left(\frac{d^2 \varphi}{d\varepsilon^2}\right)_{\varepsilon=\varepsilon_0} = \frac{1}{\overline{(\varepsilon \quad \varepsilon_0)^2}}$$

In the real ensemble (15) the mean value $\overline{(\varepsilon - \varepsilon_0)^2}$ is equal to $2k$, therefore in the real and the canonical ensemble the mean value of the squares of deviations are equal after their union a system of the same temperature. He supposes the connection performed in such a way that the two systems form together a new system, of which the reciprocal energy is small in comparison with $\varepsilon_1 + \varepsilon_2$. The connection enables the systems to interchange energy. The quantity τ of HERTZ is related to the average kinetical energy in the ensemble and is interpreted by:

$$\overline{\varepsilon_p} = \frac{n}{2}\frac{V}{\omega} = \frac{n}{2}\tau,$$

n being the number of degrees of freedom, V the volume of the extension in phase where the energy of the represented systems is less than ε, ω is put instead of $\frac{dV}{d\varepsilon}$.

HERTZ determines in a very elegant manner the conditions necessary for two microcanonical ensembles of the energies ε_1 and ε_2 and having $\tau_1(\varepsilon_1)$ equal to $\tau_2(\varepsilon_2)$ to form after their connection an ensemble of the energy $\varepsilon_1 + \varepsilon_2$ and the temperature $\tau_{12}(\varepsilon_1 + \varepsilon_2)$ so that

$$\tau_{12}(\varepsilon_1 + \varepsilon_2) = \tau_1(\varepsilon_1) = \tau_2(\varepsilon_2).$$

His considerations teach us only something about the equilibrium of temperature for stationary systems if we have shown that the average kinetical energy of a degree of freedom is equal to that in the most frequently occurring system, while the conditions of HERTZ are complied with. We shall suppose this as proved and if we then consider that two ensembles of energy ε_1 and ε_2 and of equal τ-value produce an ensemble of the same τ-value, and that the mean kinetical energy in the original ensembles is also equal and with it the kinetical energy of the most frequently occurring systems, we shall find that also the temperature of the stationary systems are equal before and after the union.

Even if we unite systems in non-stationary state, we can deduce something. If the temperature of the considered systems would be equal after they had come to a stationary state, they would belong to ensembles of equal τ. The system formed by their union belongs to an ensemble with the same value of τ, the temperature therefore adopted by the system formed if we unite two non-stationary systems is, if this system has become stationary the same as that which would have been adopted by the separate systems in their stationary state.

Also for the canonical ensemble we find the same results. GIBBS

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[1] Conf. P. HERTZ loc. cit. p. 243.

[1] For gases and fluids I have proved this in my dissertation.

has proved that the modulus Θ corresponds in all respects with the temperature. The mean value of kinetical energy in an ensemble is $\frac{n}{2}\Theta$ and this average value is equal to the corresponding value for most frequently occurring and stationary system, Θ can therefore be used to define the temperature of a stationary system.

Groningen, Dec. 1910.

Physics. — "*On vapour-pressures in binary systems with partial miscibility of the liquids.*" "VAN DER WAALS-fonds" researches N°. 2. By Prof. PH. KOHNSTAMM and Dr. J. TIMMERMANS. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of January 28, 1911).

In these Proceedings Vol. 9—11 [1]) VAN DER WAALS derived a series of conclusions concerning systems of not completely miscible liquids. In this communication we shall compare three of these conclusions with the experimental data which are to be found on this subject in the literature, and with the results of some new determinations, which follow here.

We shall discuss the three following points:

1. The shape of the p,T-projection of the three-phase curve L_1L_2G.
2. The connection between the shape of the plaitpointline and the existence of a maximum in the p,x-section of the surface of saturation.
3. The occurrence of points of inflection in the p,x-section of the surface of saturation specially in the neighbourhood of a critical end-point.

§ 1. VAN DER WAALS has tried to demonstrate that the p,T-projection of the three-phase line does not intersect the plaitpoint line in a critical end-point, but touches it. From this very remarkable results would follow.

a. In the case of splitting-up of the plaitpoint line the three-phase pressure would ascend regularly with rise of temperature. As, however, one of us [2]) remarked already before, $\frac{dp}{dT}$ has a very high value for this line in the case of splitting up of the plaitpoint line $\left(\frac{dT}{dp}\right.$ never becomes higher than 0,04 degree per atmosphere$\left.\right)$; and so the three-

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[1]) See also Archives Néerl. (2) XIII p. 249—283 (1908).

[2]) J. TIMMERMANS. Handelingen van het 13e Vlaamsche Congres 1909 p. 120.

phase pressure would have to increase very rapidly in the neighbourhood of the critical end-point.

b. In the case of retreat of the plaitpoint line, $\frac{dT}{dp}$ would be negative in the critical end-point both for the plaitpoint line and for the three-phase pressure; and as the three-phase pressure would certainly resume its usual course at lower temperatures $\left(\frac{dp}{dT}\text{ positive}\right)$ the three-phase pressure would necessarily present a maximum.

c. In the case of retreat $\frac{dp}{dT}$ of the three-phase pressure in the neighbourhood of the critical end-point could vary between a very small value (e. g. for butane + aniline: $\frac{dp}{dT} = 12.5$ atm. per degree) to infinite (e.g. for isobutane + metylalcohol); the plaitpoint temperature of this system does not appreciably vary between 10 and 70 atm.). So the latter possibility would wrongly have been considered as impossible by VAN DER WAALS[1]).

We have hardly any data as yet concerning the value of the three-phase pressures, which would enable us to test these results. Only a few observations of SCHREINEMAKERS [2]) about the system water + phenol can be used for this purpose: they have been rendered in table I.

TABLE I.

t	p in mm of mercury	$\frac{dp}{dT}$ in mm of mercury per degree
29°.8	29	
		2.26
38.2	48	
		3.33
42.4	62	
		4.05
50.3	94	
		5.16
56.5	126	
		6.66
60.1	150	
		7.44
64.4	182	
		10.45
71.2	251	
		11.32
75.0	294	

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[1]) These Proc. X p. 193.

[2]) These Proc. III p. 1. Ztschr. phys. Ch. 35 p. 459 (1900)

The critical end-point lies at 68° according to SCHREINEMAKERS; the two vapour-pressures indicated for higher temperature refer to mixtures of the critical concentration; they have been derived from VAN DER LEE [1]), who has also determined the value of $\frac{dp}{dT}$ for the plaitpoint line. This is 197600 mm. of mercury per degree, and so it is of an entirely different order of magnitude than the increase of the three-phase pressure in the neighbourhood of the critical end-point (about 10 mm. of mercury). So these data are in flat contradiction to the thesis mentioned, unless we should be ready to accept a very steep ascent of the three-phase pressure in the immediate neighbourhood of the critical end-point, where no measurements have been made, but this supposition is difficult to reconcile with the rise of the two-phase pressures of mixtures in the neighbourhood of the critical concentration, as appears from the last values of the table.

To have somewhat more material at our disposal, we have made some more determinations. Though the conclusion, being of a purely thermodynamic nature, must not depend on the nature of the system, yet we have fixed our choice on mixtures of normal substances. With the measurements we have approached the critical end-point as closely as possible. We have chosen one case of splitting up of the plaitpoint line (cyclohexane + aniline) and one of retreat (hexane and nitrobenzene), for which system the course of the plaitpoint line had been accurately determined by one of us before [2]). The substances used were very pure; we refer to the cited communication for further details.

The apparatus used is the same as had already been used by one of us [3]) for determinations of vapour-tension by a static way. A further discussion is not necessary. It was placed in a large thermostat (80 L.); the pressures were read with a kathetometer with an accuracy of 0.05 mm., after it had appeared by repeated measurement that the equilibrium had set in. The measurements (which were all made by Mr. TIMMERMANS), were first made with rising temperature, then with falling temperature; the results always agreed to 1 mm., which may be considered sufficient for the end in view. All the pressures were finally reduced to mm. of mercury at 0°. The results obtained are found in tables II and III; in the fourth column of these tables we have given the vapour pressure of the most

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[1]) Thesis for the doctorate Amsterdam 1898.

[2]) J. TIMMERMANS. These Proc. XIII p. 507.

[3]) PH. KOHNSTAMM. Thesis for the doctorate. Amsterdam 1901, p. 183. Comp also VAN DALFSEN. Thesis for the doctorate. Amsterdam 1906 p. 10.

volatile component (hexane resp. cyclohexane) at the corresponding temperature. These values have been obtained by graphical interpolation from SYDNEY YOUNG's results [1]). The fifth column at last gives the difference between the vapour pressures of the pure substances and of the three-phase system. This column clearly sets forth the perfect parallelism of the two vapour pressure curves, which gives a further support to the accuracy of the given measurements.

Here too the data for temperatures above the critical end-point refer to the two-phase pressures of mixtures of the critical concentration.

TABLE II.

Cyclohexane + aniline.

Temperature of the critical endpoint 31°.09.

$\frac{dp}{dT}$ for the plaitpoint line 166 atm. per degree.

T	p in mm. of mercury	$\frac{dp}{dT}$ in mm of mercury	p cyclohexane	D
23.22	90.65		89.4	+1 25
		4.30		
25.50	100.45		98.5	1.95
		4 37		
27.80	110.50		109.3	1.20
		5.00		
29.98	121.40		120.3	1.40
		5.19		
31.03	126.85		125.9	0.95
		4.71		
31.20	127.65		126.8	0.85
Repeated the next day:				
31.195	127.75		126.8	+0.95
		4.74		
31.100	127.30		126.3	1.00
		4.44		
30.48	124.55		123.0	1.25
		5.07		
28.99	117.00		115.1	1.90
		4.71		
27.29	108.00		106.6	2.30
		4.61		
25.61	101.15		99.2	1.95

It appears most clearly from these measurements, first that the value of $\frac{dp}{dT}$ for the three-phase pressure in the critical end-point is of a perfectly different order of magnitude from that along the plait-

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[1]) S. YOUNG and J. FORTEY. Chem. Soc. London 77 p. 1126 (1900).

TABLE III.

Hexane + nitrobenzene.

Temperature of the critical endpoint 20°.40.

$\frac{dp}{dT}$ for the plaitpoint line = 53.75 atm. per degree.

T	p in mm of mercury	$\frac{dp}{dT}$ in mm of mercury	p hexane	D
18.65	116.1		113.2	+2.9
		4.2		
19.44	119.4		117.1	2.3
		4.9		
20.24	123.3		121.4	1.9
		4.7		
20.62	125.1		123.3	1.8
15.55	103.8		98.1	5.7
		2.6		
16.52	106.3		102.6	3.7
		4.3		
17.65	111.2		108.2	3.0
		4.6		
18.65	115.8		113.2	2.6
		4.9		
19.45	119.7		117.15	2.55
18.22	115.0		111.05	3.95
		5.1		
19.05	119.2		115.2	4.0
		3.3		
19.85	121.8		119.3	2.5
		5.1		
20.30	124.1		121.7	2.4

point line, and further that both in the case of retreat and in that of splitting-up of the plaitpoint line the three-phase pressure regularly rises with the temperature to the critical end-point.

Preliminary measurements for the system isopentane + nitrobenzene have shown that neither in this case of retreat the three-phase pressure reaches a maximum, and then descends again; in consequence of an experimental accident we have failed to obtain accurate measurements on this system.

If in this way the discussed thesis about the contact of the three-phase-pressure line and the plaitpoint line appears to be incompatible with experience, we also think that we can prove that the theoretical basis of this thesis is wanting.

The $\frac{dp}{dT}$ for the three-phase pressure namely, is given by the equation

$$\frac{dp}{dT_{123}} = \frac{(x_1-x_3)(\eta_2-\eta_3)-(x_2-x_3)(\eta_1-\eta_3)}{(x_1-x_2)(v_2-v_3)-(x_2-x_3)(v_1-v_3)}.$$

We shall think the vapour phase denoted by 1, the two liquid phases by 2 and 3; now x_2 and x_3 become equal in the critical end-point, but also η_2 and η_3, and v_2 and v_3; so both the numerator and the denominator become zero. It is in this that this case distinguishes itself from the three-phase equilibrium solid-liquid-vapour, as VAN DER WAALS observes, loc. cit.[1]) because when the concentration of solid phase and liquid become equal, their volume and their entropy are not equal. We arrive at a determination of $\frac{dp}{dT}$ in the following way. The critical end-point is a plaitpoint for which the phases 2 and 3 have coincided. Now we can represent the difference of the volume and the entropy between coexisting phases in the neighbourhood of a plaitpoint by:

$$v_2 = v_3 + (x_3 - x_2)\left(\frac{\partial v}{\partial x_3}\right)_{pT} + \ldots \quad \text{and} \quad \eta_2 = \eta_3 + (x_3 - x_2)\left(\frac{\partial v}{\partial x_3}\right)_{pT} + \ldots$$

So we may put for the limit:

$$v_2 - v_3 = (x_3 - x_2)\left(\frac{\partial v}{\partial x_3}\right)_{pT} \quad \text{and} \quad (\eta_2 - \eta_3) = (x_3 - x_2)\left(\frac{\partial v}{\partial x_3}\right)_{pT}$$

If we substitute these values in the equation of $\frac{dp}{dT_{123}}$ and if we divide numerator and denominator by $x_3 - x_2$, we get:

$$\frac{dp}{dT_{123}} = \frac{\eta_1 - \eta_3 - (x_1 - x_3)\left(\frac{\partial \eta}{\partial x_3}\right)_{pT}}{v_1 - v_3 - (x_1 - x_3)\left(\frac{\partial v}{\partial x_3}\right)_{pT}} = \frac{W_{13}}{v_{13}} \quad . \quad . \quad . \quad (1)$$

On the other hand for the plaitpoint which arises by the coincidence of x_2 and x_3, the following equation holds:

$$\left(\frac{dp}{dT}\right)_{pl.\,23} = \frac{W_{23}}{v_{23}} = \frac{\eta_2 - \eta_3 - (x_2 - x_3)\left(\frac{\partial \eta}{\partial x_3}\right)_{pT}}{v_2 - v_3 - (x_2 - x_3)\left(\frac{\partial v}{\partial x_3}\right)_{pT}}$$

or if we apply again the same expansion into series as above, but take the terms with $(x_2 - x_3)^2$ into consideration:

$$\left(\frac{dp}{dT}\right)_{pl\ 23} = \frac{\left(\frac{\partial^2 \eta}{\partial x^2_3}\right)_{pT}}{\left(\frac{\partial^2 v}{\partial x^2_3}\right)_{pT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

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[1]) VAN DER WAALS. These Proc. X. p. 191.

and there is no reason whatever why (2) and (1) should be equal.

Looking back it is now easy to understand how the opposed view could assert itself. After having derived equation (1), VAN DER WAALS observes loc. cit. that this value is equal to $\left(\frac{dp}{dT}\right)_{x_3}$, i.e. the rise of the pressure when we make a section through the saturation plane $x = x_3$. And then he goes on a few lines further: "And the p,T-projection of the plaitpoint line being the envelope of the p,T-projection of the sections of the surface of saturation for constant values of x, the plaitpoint line and the p,T-projection of the sections touch and so also the final point of the p,T-projection of the three-phase pressure, as in that final point the last element of this pressure coincides with the section mentioned"[1]). From two correct premises an incorrect conclusion is drawn here. Equation (1) proves indeed that the three-phase pressure must touch the p,T-projection for x_3 constant, or in other words that the increase in pressure along the three-phase line at the limit (critical end-point) is equal to the increase in pressure of the two-phase equilibrium vapour-liquid, and this result is in perfect harmony with the data of tables I, II, and III. There is no discontinuity whatever to be seen in the value of $\frac{dp}{dT}$, when we pass the temperature of the critical end-point. It is also correct that every plaitpoint line in each of its points must touch a section for x constant through the surface of saturation (surface of two-phase equilibria), and this thesis is corroborated by equation (2). But it has been overlooked in the conclusion from these two theses that in the considered case the surface of saturation (surface of two-phase equilibria) is not a two-sheet surface, as usual, but a four-sheet one. Two of these sheets pass through the critical end-point; so instead of a mutual contact of *three* lines, as VAN DER WAALS assumed, we get a contact of *four* lines *in pairs*; the three-phase line touches the liquid sheet of the coexistence liquid-vapour, and the plaitpoint line touches one of the liquid sheets of the coexistence liquid liquid. The experimental corroboration of this last thesis is already included in the observations communicated previously by one of us[2]). For it appears convincingly from them, what moveover is a priori to be expected, that the concentration of the plaitpoint changes only exceedingly little with the temperature, and that certainly in the beginning the increase of pressure required to keep a mixture of

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[1]) Loc. cit. p. 192.

[2]) These Proc. XIII p. 507.

the concentration of the critical end-point in homogeneous state at different temperatures, may be substituted for the rise of the plaitpoint pressure proper with the temperature. And this is nothing but the thesis mentioned.

§ 2. A second thesis derived by VAN DER WAALS, which can be tested experimentally, states, that in the case of splitting up of the plaitpoint line always a minimum critical temperature of the unsplit mixture must be present, so in general also a point where the concentrations of vapour and liquid become equal (maximum vapour-pressure in the p,x-line; minimum boiling-point in the T,x-line). In the case of retreat such a point is possible, but not necessary.

In the two cases mentioned in the preceding §, the measurements seem to prove the existence of such points, because the three-phase pressure has been found higher than the value of the vapour-tension

TABLE IV.

Hexane + aniline.

Temperature of the critical end-point 68°.9.

Concentration x	weight of the aniline to 100 parts of mixture	Boiling-point	$\frac{dT}{dc}$ per %	$\frac{dT}{dx}$
0	0	68.95		
			0.170	18.04
0.0388	4.18	69.65		
			0.175	19.11
0.0859	9.31	70.55		
			0.19	20.23
0.1205	12.95	71.25		
			0.14	14.33
0.1833	19.52	72.15		
			0.08	8.32
0.2795	29.55	72.95		
			0.033	3.43
0.3524	37.04	73 20		
			0.013	1.29
0.4296	44.88	73.30		
			0.013	1.27
0.5083	52.77	73.40		
			0 007	0.72
0.5778	59.67	73.45		
			0.024	2.40
0 6403	65.80	73.60		
			0.064	6.28
0.6880	70.45	73 90		
			0.36	35.20
0.7505	76.48	76.10		
			0.74	70.83
0.8458	85.57	82.85		
			7.04	658.6
1.	100	184.40		

TABLE V.

Cyclohexane + aniline.

Temperature of the critical end-point 31°.0.

Concentration x	weight of the aniline to 100 parts of mixture	Boiling-point	$\frac{dT}{dc}$ per %	$\frac{dT}{dx}$
0	0	80.75		
			0.243	26.95
0.0167	1.85	81.20		
			0.206	22.67
0.0586	6.45	82.45		
			0.185	20.42
0.1083	11.85	83.15		
			0.127	13.53
0.2118	22.92	84.55		
			0.090	9.51
0.2749	29.55	85.15		
			0.106	11.04
0.3519	37.53	86.00		
			0.116	11.84
0.4237	44.86	86.85		
			0.119	11.98
0.4988	52.41	87.75		
			0.145	14.45
0.5576	58.25	88.60		
			0.204	20.08
0.6074	63.13	89.60		
			0.70	67.24
0.6892	71.05	95.10		
			3.8	287.3
1.	100	184.40		

of the most volatile component is according to YOUNG. But a more accurate investigation shows that this difference falls entirely within the limit of errors of the measurements. For first of all the differences between the values given by YOUNG and those given here are always very small (2 à 3 mm.), and they can be caused by traces of dissolved air, which, as is known, is exceedingly difficult to remove [1]). Then the hexane we used, was slightly less pure than that of YOUNG (too great density viz. 0.67713 instead of 0.67693 0°/4°), whereas on the other hand our cyclohexane was purer than that of YOUNG (higher melting-point 6°.50 instead of 4°.7), and these impurities are sufficient to explain the deviations.

For a further confirmation we have investigated the boiling-point line of these systems [2]). The experiments were made with BECKMANN's apparatus and with a thermometer of BAUDIN, graduated in fifths of degrees, and provided with a correction table; all the results have been reduced to the normal pressure of 760 mm. For both mixtures

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[1]) Cf. PH. KOHNSTAMM Dissertation p. 179.

[2]) Boiling point line of isopentane + nitrobenzene see Addendum p. 957.

the mixtures rich in aniline were very viscous, and showed great super-heating, which sometimes ascended as high as 25° degrees, and rendered any measurement impossible. The results have been collected in tables IV and V.

Further consideration and comparison of these data shows that we have to do here with systems interesting for more than one reason. In general the rule holds that of two substances that with the larger molecule has also the greater a, and accordingly is the less volatile one. In accordance with this most of the examined systems belong to the righthand or to the middle region of the general diagram of isobars. Now the mixtures of aniline with hexane and cyclohexane present systems with a very pronounced difference in volatility. Whereas hexane and cyclohexane have a vapour tension of 125 mm. à 150 mm at ± 33°, that of aniline is less than 0,1 mm. at that temperature [1]. Notwithstanding this aniline has the smallest b (0.006123 in the ordinary units [2]), 0.006247 for cyclohexane and 0.007849 for hexane). That in spite of this the aniline is so much less volatile is owing to this that here the a does not rise, as it usually does, and even rapidly, with increase of b, but even decreases. The a for aniline is in the same units 0,05283 to 0.05190 for cyclohexane and 0.04928 for normal hexane. So we have either systems with continually decreasing temperature of the unsplit mixture (lefthand region) or systems with a minimum T_k (middle region); in which case we are, will depend on the value of a_{12}. Now theory teaches that the existence of a point where $x_1 = x_2$ (maximum in the p,x-curve, minimum in the T,x-curve) is in the closest connection with the presence of a minimum critical temperature of the unsplit mixture. These two properties occur namely at the lowest temperatures for the same value of x; at higher temperature the mixture where $x_1 = x_2$ shifts always further to the lefthand side (smaller b, so here to the aniline-side) [3]. Now as the point $x_1 = x_2$ is not present in the boiling-point line, so at higher temperature, we must conclude for the present that really the differences in column 5 of table II must be ascribed to difference of purity between the substances investigated by us and by SYDNEY YOUNG. If a further investigation should prove the contrary, so that at lower temperature a maximum does exist, then we should meet here for the first time as far as we know with a case that is in opposition to the rule given by

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[1] KAHLBAUM. Z. phys. Ch. 26 p. 603 (1898).

[2] See LANDOLT and BÖRNSTEIN'S tables.

[3] Théorie moléculaire § 9. Cf. further VAN DER WAALS, These Proc. IV. 549 and KOHNSTAMM Z. phys. Ch. 75, p. 527 (1910).

VAN DER WAALS about the displacement of the point $x_1 = x_2$. Perhaps the best way to decide this question will be by a direct determination of the plaitpoint line $L-G$. We hope to carry it out as soon as we shall again have a sufficient quantity of cyclohexane at our disposal.

There is another circumstance which draws the attention in these systems, and which also points in the direction of a non-existence of a point $x_1 = x_2$. We refer here to the very great difference in volatility between aniline and the respective other components, of which we already spoke. At the temperatures of examination the vapour tension of hexane and cyclohexane is more than 1000 times that of aniline. Now it does not seem probable that the vapour tension of a substance could rise by the addition of a substance so much less volatile, as would be required for a maximum. In general this is even considered as so self-evident that when the two components differ very much in volatility, the validity of VAN 'T HOFF's law is generally simply accepted $\frac{dp}{pdx} = -1$, so $lim \frac{x_2}{x_1} = 0$. And this is nearly always in accordance with experience. That, however, a great difference in volatility does not always justify the supposition $lim \frac{x_2}{x_1} = 0$, the systems aniline with hexane and cyclohexane, and in a still higher degree nitrobenzene with isopentane and hexane prove, because in the latter the difference of volatility is still greater. For what conclusion we may want to draw from tables II and III concerning the existence of the maximum, this is conclusively proved by it, that the vapour pressure line descends very little from the edge if at all. Take e.g. the measurements of the two-phase pressure for a mixture of the critical concentration just above the temperature of the critical end-point. These mixtures have a concentration of about $x = 0.5$, but their vapour-pressure is not measurable lower than that of the volatile component in pure state. And compare with this e.g. the mixtures of aniline and nitrobenzene with ether examined by RAOULT [1]). Though at a concentration of 50 $^0/_0$ the vapour pressure has not diminished to half its value, as extrapolation of the rule of VAN 'T HOFF would give for these non-diluted solutions, yet the ratio found (about 3/5), differs only comparatively little from it.

It is true that a similar phenomenon as for the systems mentioned was already known for phenol and water, but the abnormality of the two components led us to suppose that this was caused by this abnormality. The three systems examined here show that also for mixtures

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[1]) Z. phys. Ch. 2 p. 353 (1888).

of normal components which differ greatly in volatility highly important deviations from the rule of VAN 'T HOFF[1]) may occur. For this it is required but also sufficient, that the value of $l = \frac{a_{12}}{\sqrt{a_1 a_2}}$ descends only comparatively little below unity (in these cases e.g. to about 0.85). This lower value of a_{12}, however, is always accompanied by a region of non-miscibility. In connection with considerations on systems of an entirely different nature one of us will shortly return to this question, and discuss it more fully; we shall therefore not dwell any longer on this point. We shall only draw one more conclusion from what has been said. If already an unusually small value of l is required to prevent $lim \frac{x_2}{x_1}$ from becoming equal to zero for mixtures of a very diverging degree of volatility, this value will of course have to be taken still smaller, if $lim \frac{x_2}{x^1}$ is put larger than 1, and so if it is assumed that the concentration of the so much less volatile component is yet greater in the vapour than in the liquid, as the existence of a maximum would require. Hence we see a corroboration in what has just been said, of the indication obtained from the boilingpoint lines that at lower temperature a point $x_2 = x_1$ does not occur in the figure either. For the same reason it seems less probable that the system sulphuric acid + decane will possess a maximum vapour pressure, though it belongs to the type of the splitting up of the plaitpoint line. [2]) From this it would follow that VAN DER WAALS's rule which states that the splitting up of the plaitpoint line always involves the occurrence of a minimum T_k is too narrow, because a point of splitting up of this line can also occur in systems from the lefthand region of the diagram of isobars, provided they do not move too far away from the region where liquid and vapour concentration become equal.

Yet an examination of all the known data shows that by far in the majority of the cases splitting up of the longitudinal plait will only occur for systems with a minimum T_k. We have collected all the experimental data in Table VI. Those concerning the plaitpoint

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[1]) Of course we do not mean here deviations for concentrated solutions, for they occur in *every* system. But we mean that VAN 'T HOFF's rule need not hold as limiting law for extreme dilution either for all mixtures which differ greatly in volatility. Moreover the condition must be fulfilled that the two substances readily mix in the liquid state, in other words that we are very far from a region of non-miscibility.

[2]) TIMMERMANS and KOHNSTAMM, These Proc. Sept. 1909, N°. 15 of the table.

TABLE VI

System.	Type			
Amylene + aniline	X	R	No maximum	D. Konowalow. Drudes Ann. 10 p. 360 (1902).
,, + nitrobenzene	X	R?	,,	
Pentane + ,,	X	R	,,	
Hexane + ,,	X	R	,, ?	This communication.
,, + aniline	X	R	,, ?	
Cyclohexane + aniline	X	S	,, ?	
Ethane + methylalcohol	X	L	,,	J. P. Kuenen and W. G. Robson. Phil. Mag. (5) 48 p. 180 (1899).
,, + ethyl ,,	X	L	,,	
,, + propyl ,,	X	L	,,	
,, + butyl ,,	X	L	,,	
Carbonic acid + o-nitrophenol	X	L	,,	Büchner. Thesis. f. the doctorate Amst. (1905).
Nicotine + water		L	,,	Schukarew. Z. phys. Ch. 71 p. 100 (1910).
Chloric hydrate + water	X	L?	,, (Minimum)	Van Rossem. Z. phys. Ch. 62 p. 681 (1908).
Sulphur + toluol	X	R?	No maximum	J. K. Haywood. J. of phys. Ch. 1. p. 232 (1897).
,, + xylol	X	R?	,,	
Ether + water		L?	Maximum	J. P. Kuenen and W. C. Robson. Z. phys. Ch. 28. p. 349 (1899).
Water + phenol	X	S	,,	F. A. H. Schreinemakers. Z.phys. Ch. 35. p. 459 (1900)
,, + aniline		S	,,	
,, + isobutylalcohol		R	,,	D. Konowalow. Wied. Ann. 14. p. 34 (1881).
,, + iscamylalcohol		R	,,	
,, + butyric acid		R	,,	
,, + isobutyric acid		R	,,	
,, + isovaleric acid		R	,,	
,, + sec. butylalcohol		R	,,	J. Timmermans.
,, + methylethylketone		R	,,	
,, + acetylacetone		R	,,	Schukarew. Z. phys. Ch. 71 p. 100 (1910).
,, + triethylamine		L	,,	
Propane + methylalcohol		R	,,	J. P. Kuenen. Phil. Mag. (6) 6 p. 637 (1903).
Isopentane + ,,		S	,,	
Hexane + ,,		S	,,	
Cyclohexane + ,,		S	,,	Lecat. Diss. Brussel 1908.
Carbon disulphide + methylalcohol		S	,,	G. Ryland. Amer. Ch. J. 22. p. 384 (1899).
,, + acetone		S?	,,	
Benzene + formic acid		S	,,	W. Nernst. Z. phys. Ch. 8. p. 110 (1891).

line have been derived from our preceding communication; those concerning the vapour-pressure-lines are spread in the literature; we have referred to the original in every case. The cases of splitting up are marked by an *S*, those of retreat by an *R*, lower critical end-points by an *L*. The sign *X* indicates that the concentration of the vapour phase falls outside that of the liquid phases. A note of interrogation marks doubtful cases. We have also inserted the only case known of a minimum vapour pressure being attended by unmixing; as is known it is almost certain that for these systems there exist compounds between the components.

§ 3. The last point we want to discuss is the occurrence of points of inflection in the p,x-line specially in the neighbourhood of a critical endpoint. As has been set forth at length by KUENEN[1]), in the critical end-point these lines possess a point of inflection with horizontal tangent. So above the critical end-point (we suppose it to be an upper mixing-point) there will continue to exist a point of inflection in the neighbourhood of the critical concentration, but the tangent is no longer horizontal in this point of inflection. This shape of the p,x-line is in close connection with a similar shape of the boiling-point or the melting-point lines in the neighbourhood of a critical end-point. With regard to the shape of the melting-point lines we possess important systematic investigations by FLASCHNER and RANKIN[2]).

Concerning the boiling-point and the vapour tension lines of this

TABLE VII.
Temp. of the crit. end-point.

System	T_1	T_2	Observer
Amylene + aniline	1°.5	18°.1	D. KONOWALOW. Drudes Ann. 10 p. 360 (1902).
Isopentane+dichloroacetic acid	<0	0	D. KONOWALOW. J. de Ch. ph. p. 1 (1907).
Hexane + aniline	68.9	73.4	This communication.
Cyclohexane + „	31.8	85.5	
Hexane + methylalcohol	43	43.8	A. SCHUKAREW. Z. ph. Ch. 71. p 100 (1910).
Water + phenol	68	71.2	F. A. H. SCHREINEMAKERS. Z. ph. Ch. 35. p. 456 (1900).
„ + acetylacetone	91	91.2	SCHUKAREW.
„ + nicotine L	60	59.6	

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[1]) Verdampfung und Verflüssiging von Gemischen. Leipzig Barth 1906 p. 170.

[2]) O. FLASCHNER and J. G. RANKIN Monatshefte f. Ch. 31 p. 23 (1910).

kind we have comparatively few data as yet: we have collected what is known of it, in table VII. The second column (T_1) gives the temperatures of the critical end-point, the third that at which the point of inflection is observed.

It is seen that the existence of points of inflection in these lines in the neighbourhood of critical end-points is of general occurrence, also when the two components are normal non-associating substances. In the system aniline + cyclohexane it even exists up to 50° above the critical end-point. If we wished to insert all the known cases of points of inflection into the table, also when the measurement was made far from the critical end-point, a great number might probably be added to the list. It is indeed difficult to see how one should conceive the course of these p,x-lines without points of inflection. Already in 1901 one of us[1] drew attention to the existence of points of inflection in the p,x-lines of ether[2]) with little volatile substances in opposition to a thesis of OSTWALD, who denies the possibility of such points of inflection for the general case, so even for components which associate in the liquid phase or act chemically upon each other[3]). The systems mentioned here are new proofs which refute this thesis.

But they prove more. As one of us derived lately from the theory of VAN DER WAALS, p,x-lines with *two* points of inflection are to be expected under certain circumstances. There he only showed under what circumstances a p,x-line will occur which is convex downward on the two sides, concave in the middle, and adds to this: "Den umgekehrten Fall, eines konvexen Teiles zwischen zwei konkaven, den man erhalten wird wenn $l_6 < l_7$, habe ich bis jetzt noch nicht gefunden, doch es ist kein Grund mehr vorhanden, ihn als unmöglich zu betrachten." The measurements published here about the system hexane and aniline confirm the rule found theoretically. For if we try to draw up a p,x-line for e.g. 73.°30 from the data of table IV, we can hardly give it another shape than the one just described Direct experimental determination of the p,x-line itself, however, remains desirable.

At any rate there is now one reason more for the warning given loc. cit., that from the somewhat divergent course of the p,x-lines from the prevailing type we are not yet justified in concluding to the existence of a dissociating compound, as is often done. In the

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[1]) PH. KOHNSTAMM. Z. phys. Ch. 36 p. 41 (1901).

[2]) RAOULT, Z. phys. Ch. 2 p 353 (1888).

[3]) Lehrbuch der allgemeinen Ch. II 2 p. 642.

[4]) PH. KOHNSTAMM. Z. phys. Ch. 75 p. 550 (1910).

system hexane and aniline we are saved from this error by the circumstance that its critical end-point can be realised, but it is of course very well possible that in other cases the appearance of the crystalline phase prevents this realisation. Only the determination of the melting-point line can give certainty in such cases.

How the facts mentioned here, and indeed so many others could be made to harmonize with the "theory" which was advocated many years ago by SPEYERS [1]), and which has been upheld again of late by DOLEZALEK [2]), according to which the partial pressures of the components are always proportional to the liquid concentration, is not to be understood. Even if we restrict ourselves to mixtures of normal substances, the abundance of phenomena is so great that it can only be accounted for by a theory which takes account of the great difference which can exist in the three quantities which together determine the state of such a binary mixture: the ratio of the molecular size $n = \frac{b_2}{b_1}$, the ratio of the molecular attraction $k = \frac{a_2}{a_1}$, and the attraction inter se of the molecules $l = \frac{a_{12}}{\sqrt{a_1 a_2}}$.

CONCLUSIONS.

We have demonstrated in this communication:

1. That the expectation pronounced by VAN DER WAALS that the line of the three-phase pressures $L_1 + L_2 + G$ would touch the plaitpoint line in the critical end-point is in contradiction with the experiment, but that also further theoretical consideration proves this expectation to be unfounded, and gives two other rules which are both confirmed by the experiment instead of VAN DER WAALS' thesis.

2. That in general the rule given by VAN DER WAALS that splitting up of a plaitpoint line only occurs in systems from the middle region of the diagram of isobars, is corroborated by experience. But that nevertheless also cases seem to occur in which systems from the lefthand region of the diagram of isobars (descending T_k with ascending b without the minimum T_k being reached) present splitting up of the plaitpoint line. Also for other above mentioned reasons a further investigation of these mixtures remains very desirable.

3. That in opposition to the theories of OSTWALD, SPEYERS, DOLEZALEK, and others, but in agreement with the theory of VAN DER WAALS mixtures of normal substances can possess p,x-lines with a point of inflection, and even with more than one, when we approach the region of non-miscibility.

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[1]) Journ. of Phys. Chem. 2 p. 347, 362 Journ. Amer. Ch. Soc. 21 p. 312, 725.

[2]) Zeitschr. f. Phys. Ch. 62, 727; 71, 191.

Physics. — "*Selective absorption and anomalous scattering of light in extensive masses of gas.*" By Prof. W. H. Julius.

(Communicated in the meeting of January 28, 1911).

§ 1. *Resonance and damping.* — The dispersion of light is at present generally explained by supposing the molecules of the medium to contain electrons, bound to positions of equilibrium by quasi-elastic forces. Such electrons have their own period of vibration T; their motion will continually increase by resonance, if in the incident beam of light there are waves of the same period. As light, somewhere in the visible spectrum, may give impulses at the rate of 500 billion a second to a resonant electron, one conceives that in a very short time the amplitude of the electron will considerably increase, even though the impulses may be weak.

Waves of a slightly different period T' are also able to set the same electrons moving; they force the period T' upon them; but the resulting amplitude of the forced vibration is the smaller, the greater the value of $\pm (T - T')$. The absorption spectra of gases will appear, however, to be only slightly affected by this phenomenon. We may refer to a general result obtained by Helmholtz[1]) as to how the intensity of the forced vibrations of a system is determined by the rate of extinction of the free vibrations, and the difference of the periods, $T - T'$. If the extinction is slow, sensible amplitudes are not reached unless T' differs *very* little from T. Now we know from the phenomena of interference with great differences of path, that the free vibrations of electrons are so little subject to damping, as to have more than $^1/_{10}$ of their energy left after 300.000 vibrations have been accomplished. Applying Helmholtz's formula to the case, we find, that the energy of the forced vibrations of period T' will be smaller than $^1/_{10}$ of the energy of the exactly resonant vibrations of period T, if the wave-lengths corresponding to those two periods differ as little as 0,01 Å. So the width of the region of sensible co-vibrating scarcely exceeds some 0,02 Å.

The amplitude of a resonant electron cannot, of course, go on increasing infinitely, and no doubt the quasi-elastic force will cease from being proportional to the displacement when the latter has become very great. As soon as the amplitude surpasses a certain value, the electron will be strained out of the molecule and set to moving independently: then radiation has led to ionisation. But

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[1]) Helmholtz, Die Lehre von den Tonempfindungen (1877), S. 233 und 642.

absorption of light is not always accompanied by ionisation; in most cases the above-said critical value evidently is not exceeded, which means that some cause must exist by which the increase of the amplitude is limited. Such a cause is formally accounted for by introducing a "resistance", which opposes the motion of the electron and is supposed to be proportional to its velocity. The equations of motion of an electron, moving under the influence of a (periodically changing) electric force (XYZ), therefore have the form

$$m\frac{d^2x}{dt^2}+h\frac{dx}{dt}+kx=eX, \text{ etc.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where m means the mass, e the charge of the electron, while the magnitude of the quasi-elastic force is determined by k, that of the resistance by h.

We propose to study in this paper the nature of the damping parameter h, and to inquire into the influence which the damping forces exert on the intensity of light propagated through very extensive gaseous media, like the atmospheres of the sun and the stars.

§ 2. *Recalling some results of the dispersion theory.* — We know that the dispersion theory answers the question, how a given periodically changing electric force is propagated through a medium containing a large number of electrons, the motion of which is represented by a set of equations of the above form [1]).

Let the medium contain $\mathfrak{N}$ similar molecules per unit of volume, each of them furnished with a few differently connected electrons, so that there are a limited number of periods of free vibrations; then we only have to apply the general equations of the electromagnetic field to this charged medium, and, using the notation introduced by W. Voigt [2]), which is well adapted to our purpose, we find the following solution:

$$\mathfrak{n}^2=n^2(1-i\varkappa)^2=1+\Sigma\frac{4\pi\mathfrak{N}\frac{e^2}{m}}{\frac{k}{m}+i\frac{h}{m}\mathfrak{r}-\mathfrak{r}^2}=1+\Sigma\frac{\varrho}{\mathfrak{r}_0{}^2+i\mathfrak{r}'\mathfrak{r}-\mathfrak{r}^2} \quad . \quad (2)$$

In this equation $\mathfrak{n}$ represents the complex index of refraction,

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[1]) The equations of motion of the electron with which Lorentz starts (The Theory of Electrons, p. 139) contain two additional terms, and, therefore, are more general than the set (1). In the problem of which we are going to treat, we may omit those terms, because 1st we need not account for an exterior magnetic field, and 2nd we only wish to apply our results to media of low density.

[2]) W. Voigt, Magneto- und Electro-optik, (1908) p. 107.

n the real index of refraction, $\varkappa$ the index of extinction, while $\mathfrak{r}$ means the frequency (i.e. the number of vibrations in the time 2π) of the kind of light we are considering. The meaning of ϱ, $\mathfrak{r}_0$ and $\mathfrak{r}'$ is clear from the formula. That $\sqrt{\frac{k}{m}} = \mathfrak{r}_0$ is the frequency of the "free vibration" of the electron becomes apparent, if in equation (1) we put $h = 0$ and $X = 0$, which means that no damping and no external electric force are supposed to exist. Each kind of electrons contributes a term in the sum.

Separating the real from the imaginary terms in (2) leads to the relations

$$\left.\begin{aligned} n^2(1-\varkappa^2) &= 1 + \Sigma \frac{\varrho(\mathfrak{r}_0^2-\mathfrak{r}^2)}{(\mathfrak{r}_0^2-\mathfrak{r}^2)^2+\mathfrak{r}'^2\mathfrak{r}^2} \\ 2n^2\varkappa &= \Sigma \frac{\varrho\mathfrak{r}'\mathfrak{r}}{(\mathfrak{r}_0^2-\mathfrak{r}^2)^2+\mathfrak{r}'^2\mathfrak{r}^2} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (3)$$

from which n and $\varkappa$ have to be solved. This problem becomes much simpler, and yet scarcely less general, if we confine our attention to the surroundings of each of the characteristic frequencies $\mathfrak{r}_0$ separately. In equation (2) we therefore put apart the term relating to the selected $\mathfrak{r}_0$, and designate the other terms of the sum by a variable index h:

$$n^2 = 1 + \Sigma \frac{\varrho_h}{\mathfrak{r}_h^2 + i\mathfrak{r}'_h\mathfrak{r} - \mathfrak{r}^2} + \frac{\varrho}{\mathfrak{r}_0^2 + i\mathfrak{r}'\mathfrak{r} - \mathfrak{r}^2} \quad . \quad . \quad . \quad . \quad (4)$$

Because we only consider such values of $\mathfrak{r}$ as differ little from $\mathfrak{r}_0$, we are allowed to replace $\mathfrak{r}$ by $\mathfrak{r}_0$ in the terms of the summation Σ, and then to neglect $i\mathfrak{r}'_h\mathfrak{r}_0$ relatively to $\mathfrak{r}_h^2 - \mathfrak{r}_0^2$ (the damping connected with $\mathfrak{r}_h$ being imperceptible near $\mathfrak{r}_0$). Writing $\mathfrak{r} - \mathfrak{r}_0 = \mu$, and therefore ($\mu$ being small) $\mathfrak{r}^2 - \mathfrak{r}_0^2 = 2\mathfrak{r}_0\mu$, we may put, instead of (4):

$$n^2 = 1 + \Sigma \frac{\varrho_h}{\mathfrak{r}_h^2 - \mathfrak{r}_0^2} - \frac{\varrho}{\mathfrak{r}_0(2\mu - i\mathfrak{r}')}$$

or

$$n^2 = n_0^2 - \frac{\varrho}{\mathfrak{r}_0(2\mu - i\mathfrak{r}')}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where n_0 represents the value which, in the small spectral region we are considering, the index of refraction would show if there were no electrons having the proper frequency $\mathfrak{r}_0$.

One might proceed to the separation of the real from the imaginary part of this simplified equation, and then solve n and $\varkappa$; but as the result would not yet be very simple, we shall first consider the special case that the modulus of the complex second term is small compared with n_0^2, for all values of μ lying within the region we are concerned with. Then $n^2 - n_0^2$ may be replaced by $2n_0(n - n_0)$, and separating the real from the imaginary part, we find:

$$n = n_0 - \frac{\varrho\mu}{n_0\mathbf{r}_0(4\mu^2 + \mathbf{r}'^2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

$$n\varkappa = \frac{\varrho\mathbf{r}'}{2n_0\mathbf{r}_0(4\mu^2 + \mathbf{r}'^2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6a)$$

which formulae easily show the symmetry of the curves representing n and $n\varkappa$ as functions of μ.

As to n, it is clear indeed that $n = n_0$ for $\mu = 0$, and that for some positive value of μ (i.e. on the violet side of $\mathbf{r}_0$) n is smaller than n_0 by a certain amount, while for an equal negative value of μ (on the red side) n is larger than n_0 by the same amount. For $\mu = -\,^1/_2\,\mathbf{r}'$, n reaches a maximum:

$$n = n_0 + \frac{\varrho}{4\,n_0\mathbf{r}_0\mathbf{r}'},$$

and for $\mu = +\,^1/_2\,\mathbf{r}'$ a minimum:

$$n = n_0 - \frac{\varrho}{4\,n_0\mathbf{r}_0\mathbf{r}'}.$$

The attenuation coefficient $n\varkappa$ has its greatest value $\frac{\varrho}{2\,n_0\mathbf{r}_0\mathbf{r}'}$ at the point $\mu = 0$; passes the value $\frac{\varrho}{4\,n_0\mathbf{r}_0\mathbf{r}'}$, which is half that of the maximum, at $\mu = \pm\,^1/_2\,\mathbf{r}'$, i.e. exactly there where the maximum

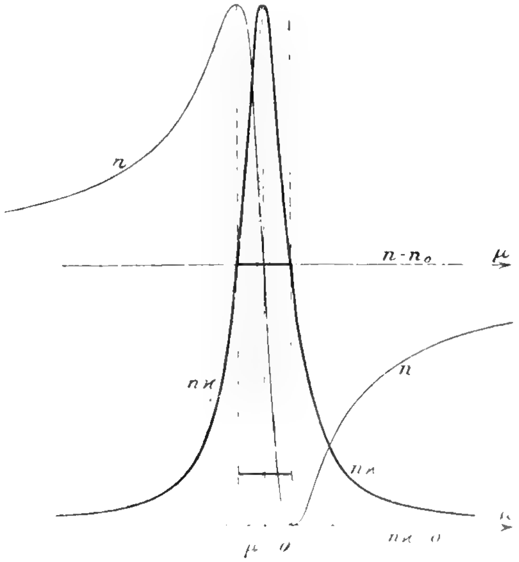

Fig. 1.

and the minimum of n are found; and, with increasing μ, approaches zero on both sides. Fig. 1 (taken from VOIGT l.c. p. 115) shows the curves representing the two functions. We may consider $\mathfrak{r}'$ as measuring the width of the dark line appearing in the spectrum. Indeed, the slope of the intensity curve is much steeper than the slope of $n\varkappa$, because the strength of the transmitted light (provided we are not dealing with the radiation through a thick atmosphere, cf. § 5) is given by $I = I_0 e^{-\frac{4\pi}{\lambda} n\varkappa z}$, z being the length of the path through the gas. The dotted curve represents the reciprocal value of the intensity of the transmitted light on the supposition that for $\mu = 0$ we have $I = {}^1/_{100}\, I_0$, so that at $\mu = \pm {}^1/_2\, \mathfrak{r}'$, where $n\varkappa$ has half its maximum value, we find $I = {}^1/_{10}\, I_0$. Almost the whole of the dark line thus lies between $\mu = -{}^1/_2\, \mathfrak{r}'$ and $\mu = +{}^1/_2\, \mathfrak{r}'$ [1]).

§ 3. *Cases in which the anomaly of the dispersion curve is greater.* Our object being to apply the results of the theory to the interpretation of the solar spectrum, we must allow for the possibility that perhaps not in all cases the modulus of $\frac{\varrho}{\mathfrak{r}_0(2\mu - i\,\mathfrak{r}')}$ may be taken to be small as compared with n_0^2 (e.g. when we are concerned with very strong lines, like the calcium lines H and K); we therefore return to equation (5). Separating the real from the imaginary part, we obtain

$$n^2 - n^2\varkappa^2 - n_0^2 = \frac{-2\varrho\mu}{\mathfrak{r}_0(4\mu^2 + \mathfrak{r}'^2)}, \text{ and } n^2\varkappa = \frac{{}^1/_2\,\varrho\mathfrak{r}'}{\mathfrak{r}_0(4\mu^2 + \mathfrak{r}'^2)}.$$

The substitution of the second equation into the first one leads to

$$n^2 - n_0^2 = \frac{-2\varrho\mu + {}^1/_2\,\varrho\mathfrak{r}'\varkappa}{\mathfrak{r}_0(4\mu^2 + \mathfrak{r}'^2)} \quad \text{or} \quad n - n_0 = \frac{-\varrho\mu + {}^1/_4\,\varrho\mathfrak{r}'\varkappa}{{}^1/_2(n + n_0)\mathfrak{r}_0(4\mu^2 + \mathfrak{r}'^2)} \qquad (7)$$

from which we deduce

$$n = n_0 + \frac{{}^1/_4\,\varrho\mathfrak{r}'\varkappa}{{}^1/_2(n + n_0)\,\mathfrak{r}_0(4\mu^2 + \mathfrak{r}'^2)} - \frac{\varrho\mu}{{}^1/_2(n + n_0)\,\mathfrak{r}_0(4\mu^2 + \mathfrak{r}'^2)}. \qquad (8)$$

A similar position as, according to (6), the curve n takes with respect to the straight line n_0, it assumes according to (8) with respect to the curve $n_0 + d$ (if d represents the second term, which is variable with n and $\varkappa$). By that term d the character of the curve n is, however, scarcely influenced, because ${}^1/_4\,\mathfrak{r}'\varkappa$ is small in com-

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[1]) We shall see later on that in the light which has traversed the *solar atmosphere*, the apparent width of the real absorption lines must be even less, because part of the attenuation depends on scattering, and this part follows a law different from the exponential one.

parison with μ. Even within the region of strong absorption, the term δ is of little consequence. Let us for instance consider the frequency where $\mu = {}^1/_2\, r'$. There the ratio of the second to the third term is

$$ {}^1/_4\, r'\varkappa : \mu = {}^1/_4\, r'\varkappa : {}^1/_2\, r' = {}^1/_2\, \varkappa . $$

There are no experimental data at my disposal from which the values of $\varkappa$ might be deduced for calcium vapour; but for sodium vapour the maximum value of $n\varkappa$ was found to be 10^{-3} [1]), which, at the indicated spot of the spectrum, makes $n\varkappa = 5 \times 10^{-4}$, and, consequently, ${}^1/_2\varkappa = {}^1/_n \times 2{,}5 \times 10^{-4}$. For greater values of $\pm\mu$ the said ratio decreases rapidly. So the second term of the second member of (8) may be neglected.

But in the denominator of the third term we meet with the variable factor ${}^1/_2\,(n + n_0)$, where in (6) the constant factor n_0 occurs. It follows from this circumstance that now the dispersion curve does not show the perfect symmetry of the one which represents equation (6). The character of the deviation becomes apparent from equation (7) if, omitting the term ${}^1/_2\, \varrho r'\varkappa$, we write:

$$ n^2 = n_0^2 - \frac{2\varrho\mu}{r_0\,(4\mu^2 + r'^2)} . $$

With respect to the point of intersection P of the horizontal line n_0^2 (fig. 2) with the vertical line $\mu = 0$ the curve representing n^2 is symmetrical. Let us now suppose $n_0 = 1$, then the line n_0 coincides with the line n_0^2. Constructing, in the same figure, the curve whose ordinates are the square roots out of the ordinates of the first curve, we immediately see, that the "anomaly" of the index of refraction n is greater on the violet than on the red side of the line. It is questionable whether absorbing vapours will present cases in which this difference is great enough to show itself in the observations.

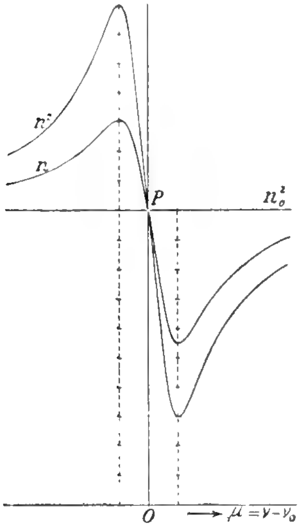

Fig. 2.

§ 4. *On the nature of the damping parameter.* — A permanently acting cause why the vibrations of an electron die out, is the fact that it radiates waves in all directions, thus "scattering" its kinetic energy. An electron, moving with the variable velocity v, experiences a force due to its own field, opposite to its acceleration, and, in

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[1]) W. VOIGT, l. c. p. 142.

first approximation, proportional to $\frac{dv}{dt}$; this accounts for the inertia. But the force also contains a term, proportional to $\frac{d^2v}{dt^2}$, viz: [1])

$$r = \frac{2}{3}\frac{e^2}{c^3} \cdot \frac{d^2v}{dt^2}.$$

If now the motion is periodical: $v = b \cos \nu t$, we shall have $\frac{d^2v}{dt^2} = -\nu^2 v$, so that we may put

$$r = -\frac{2}{3}\frac{\nu^2 e^2}{c^3} \cdot \frac{dx}{dt}$$

where x means the elongation at the time t.

This term of the force may therefore be considered to express a "resistance", being proportional to the velocity and having the opposite direction. The numerical value of the coefficient is small: and that the resulting attenuation of the vibrations really is insignificant, appears from the known phenomena of interference with great differences of path, which show that after some 100000 vibrations the amplitude of an electron has scarcely diminished. On the basis of this cause of damping we are not able to account for the *absorption* of the incident light, i.e. for a transformation of the radiant energy into heat or other forms of energy. The scattered light remains radiant energy of the vibration periods occurring in the original beam of light.

In order to explain absorption, LORENTZ assumes, that the vibrations of an electron excited by incident waves of light, go on undisturbed only during a certain interval of time τ, and that then, for instance in consequence of the collisions of the molecules, their energy is transformed and distributed among other systems. [2]) This idea may be expressed mathematically by giving the damping parameter h the value $\frac{2m}{\tau}$. It is not necessary, however, to identify τ with the mean length of time elapsing between two successive collisions of a molecule; indeed, after a much shorter interval τ the amplitude of a resonant (or almost resonant) electron might already have increased to such a value, that also the other components of the molecule to which it belongs have been thoroughly shaken, and have assumed

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[1]) LORENTZ, The theory of electrons, p. 49; Encyklopädie der math. Wiss. V. 2, 188; ABRAHAM, Theorie der Electrizität II, S. 72, 123. In the above formula e is expressed in the C. G. S. unit reposing on COULOMB's law.

[2]) LORENTZ, The theory of electrons, p. 141.

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part of its energy. In that case we are already witnessing an "absorption" process; the further transformation of the energy into heat, etc. ensues by collisions.

According to this conception, *absorption* of radiant energy only takes place, when by resonance certain electrons are set vibrating to such a degree, that energy is imparted by them in an irreversible way to other parts of the systems to which they belong. As to the particular conditions of this process, we can only guess at them. LORENTZ has shown 1) that the damping influence of *collisions* may approximately be expressed by introducing into the equations of motion a term, proportional to the velocity of the electron. But if the absorption process already begins within the molecule, before a new encounter takes place (as LORENTZ thinks probable, l. c. p. 142), it is quite conceivable that the amplitude, and, therefore, the velocity of the resonant electron must have increased beyond a certain limit, before a continual transfer of energy to other parts of the same molecule can result 2). If the connections really are of that kind, then waves which on account of imperfect resonance impart only *small* mean velocities to the electron, will suffer *no absorption at all*: the part of the damping parameter that is due to absorption, will sink to zero at a certain small distance on both sides of the centre of the absorption line. This, of course, is an hypothesis to which, in the absence of a deeper knowledge of the internal structure of the molecules, we are unable to give a solid foundation, but which may be put to the test by scrutinizing the deductions following from it.

Suppose a beam of white light to pass through a rarefied gas having rather sharply defined periods of free vibrations 3), then, according to § 1, the spectral region in which effectual co-vibrating occurs, is only little wider — for each kind of electrons — than

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1) LORENTZ, l, c. Note 57.

2) This conception agrees very well with a new radiation hypothesis, recently proposed by PLANCK (Verhandl d. Deutschen physikalischen Gesellschaft 13, p. 138), according to which *accumulating* radiant energy by resonance is a continuous process, whereas *emitting* radiant energy only takes place by definite "light-quanta". — Now, let the forced vibrations of an imperfectly resonant electron attain an intensity sufficient for it to emit light-quanta by itself, but not sufficient to shake the other electrons, belonging to the same molecule (and having frequencies of their own), to such a degree as would be necessary for them also to emit quanta: then part of the incident radiation is *scattered* by the electron first affected, but there is no *absorption*, no transformation of the accumulated energy into energy of some other kind.

3) The proper periods are never defined with *perfect* sharpness, owing to the disturbing influence of collisions and to the DOPPLER-effect.

the region of their proper periods; but, strictly speaking, co-vibrating takes place in some degree throughout the spectrum, though with decreasing intensity as one recedes from the line corresponding to the free vibration. Now, according to our hypothesis, the same cannot be said with regard to *absorption*, this process being confined to a narrow part of the region of resonance.

Let us consider the share which *scattering* has in the act of damping. Within the region of strongest absorption it keeps in the back-ground: indeed, for sodium light the factor $\frac{2\mathrm{r}^2 e^2}{3c^3}$ amounts to only 2×10^{-20}, while the value of the entire damping parameter in sodium vapour was found to be: $h = m\mathrm{r}' = 7 \times 10^{-28} \times 11.2 \times 10^{10} = 7.8 \times 10^{-17}$ [1]. But on the other hand, we have no ground to doubt, as in the case of absorption, the proportionality of this damping effect to the velocity, however small it may be[2]. Scattering extends all over the spectrum, wherever the proper frequencies of the electrons may be found.

Indeed, apart from the theory of absorption and dispersion RAYLEIGH has proved that a beam of light of intensity J_0 and wave-length λ, after having travelled a distance x through a mass of gas whose index of refraction is n, and which contains N scattering molecules per unit volume, will have sunk to the intensity

$$J = J_0 \, e^{-\frac{32\pi^3(n-1)^2}{3\lambda^4 . N} x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The quantity $s = \frac{32\pi^3(n-1)^2}{3\lambda^4 . N}$ is called the *coefficient of scattering*.

Let Δ be the density of the gas, then $\frac{n-1}{\Delta} = R$ may be considered constant for any given wave-length. As we may put Δ proportional to N, say $\Delta = f . N$, the expression $\frac{n-1}{N} = f . R$ is also a constant for any definite kind of light. Introducing it into the coefficient of scattering, we find

$$s = \frac{32\,\pi^3\, N f^2\, R^2}{3\lambda^4} = \frac{32\,\pi^3\, \Delta . f . R^2}{3\lambda^4} \quad . \quad . \quad . \quad . \quad (10)$$

where R represents the *refraction constant* of the medium.

The coefficient of scattering is thus inversely proportional to the

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[1] From observations by HALLO, concerning the magnetic rotation of the plane of polarisation in sodium vapour, VOIGT calculated: $\nu' = 11{,}2 \times 10^{10}$. Cf. VOIGT, l. c. p. 142.

[2] If we admit PLANCK's new radiation hypothesis, this statement will have to be corrected.

fourth power of the wave-length, direct proportional to the density, to the average mass contained in the medium per scattering particle and to the square of the refraction constant. As the latter varies strongly in the neighbourhood of a proper frequency, also if the damping parameter is small or even approaches zero (Cf. VOIGT, l.c. p. 118), the coefficient of scattering will assume widely different, and relatively great values in such a region; it only vanishes for waves travelling in the medium with the same velocity as in the ether, i.e. in places of the spectrum where $R = 0$, or $n = 1$.

The effect of absorption and scattering may be considered from two points of view. First we may inquire into the influence of these two damping causes on the motion of the electrons, and, consequently, on the optical properties of the medium (as characterized by n and $\varkappa$). The second point of view is that in which, the incident light being given, we desire to study the intensity and the composition of the light that leaves the absorbing medium.

So far we have only considered the first question. We concluded that for waves, belonging to the nearest vicinity of those corresponding to the free vibrations of a gas, the damping parameter h must be the sum of two terms:

$$h = \frac{2m}{\tau} + \frac{2}{3}\frac{\mathbf{r}^2 e^2}{c^3}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

that in the middle part of that narrow region the first term is great compared with the second one; that very probably, however, the value of the first term sinks rapidly to zero at a short distance from each of the proper frequencies, so that in the rest of the spectrum it is only the effect of the second term which remains.

The parameter h, therefore, is not a constant, even if we confine our attention to a part of the spectrum so small, that the variation of the factor $\mathbf{r}^2$ may be neglected. Nevertheless, our fig. 1 (p. 884) gives the principal features of the index of refraction as a function of the frequency, with a fair degree of exactness, because the character of the dispersion curve is much the same for different values of h. The relation, for instance, that the maximum and the minimum of n are found where $\mu = \pm \, ^1/_2 \, \mathbf{r}'$, will continue to hold, if at these points of the spectrum the second (constant) term of h already prevails. But if at the points where μ passes the values $\pm \, ^1/_2 \, \mathbf{r}'$, the function $\mathbf{r}'$ (or h) increases rapidly with decreasing absolute value of μ, then the distance between the maximum and the minimum of n must be greater than $\mathbf{r}'$.

§ 5. *Radiation through an extensive atmosphere.* — We shall now proceed to a discussion of the second question, that which regards the composition and properties of the light that has traversed a very thick layer of gas, the atmosphere of a celestial body, if we suppose the emission curve of the original source of light to be continuous.

Evidently the solution cannot be found by simply putting the value

$$\nu' = \frac{h}{m} = \frac{2}{\tau} + \frac{2}{3}\,\frac{\nu^2 e^2}{c^3 m}$$

into the formulae (3) or (6*a*), and then, for each wave-length separately, substituting the resulting value of $n\varkappa$ into an equation of the form

$$I = I_0\, e^{-\frac{4\pi}{\lambda} n\varkappa \, . \, z} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12$$

(in which z represents the distance travelled by the beam through the layer of gas).

For this would lead to an entirely erroneous result, even if the layer of gas were perfectly homogeneous. It is true that the part of the attenuation, which is due to *absorption*, conforms to the law expressed by (12), proceeding in a geometrical progression when the path through the gas increases in an arithmetical progression; but the same does not apply to the part that is caused by *scattering*. If the source of light and the layer of gas are very extensive, we must take into consideration that each electron emits a certain quantity of scattered light owing to irradiation from all directions, and partly joining the directly transmitted beam. The attenuation of the beam must therefore proceed less quickly than it would do according to the law expressed by (12), which holds for the loss of intensity by absorption [1]).

SCHUSTER [2]) was the first to discuss in an ample way the combined influence of scattering, absorption, and emission of light in extensive masses of gas. Basing his conclusions on KIRCHHOFF's law, and making various suppositions as to the ratio between the coefficients of absorption and scattering, he examined into the circumstances that would make an atmosphere of a certain depth produce either dark or bright spectral lines.

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[1]) RAYLEIGH, in deducing the formula (9), has not taken this into consideration; his result only applies to the attenuation which the original beam suffers by scattering, and does not include the scattered light itself.

[2]) SCHUSTER, Radiation through a foggy atmosphere. Astroph. Journ. **21**, p. 1, (1905).

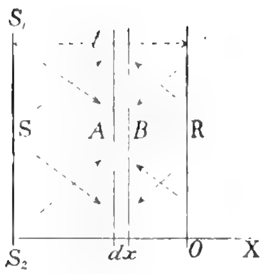

Fig. 3

The way of attacking the problem was as follows. Let an atmosphere of thickness l be irradiated by a surface S_1S_2 (fig. 3), which per unit emits a quantity of energy S within the limit of wave-lengths λ and $\lambda + d\lambda$, and uniformly distributed over all directions. Now SCHUSTER begins with calculating the change which the total flow of radiant energy suffers in a thin layer dx of that atmosphere. The layer receives from the left a quantity A per unit surface (which in general must be smaller than S, although it includes, besides the radiation directly coming from S_1S_2, also the radiation emitted by the part of the atmosphere lying between S_1S_2 and the layer dx). Of this quantity A the layer absorbs $\varkappa A dx$[1]), and scatters $sAdx$, the latter part not being lost as radiant energy of the given wave-length, but proceeding half to the right, half to the left. From the right side the layer receives a quantity of energy B per unit surface (composed of scattered light and proper radiation due to the outer part of the atmosphere); it absorbs $\varkappa B dx$ and scatters $sBdx$, of which $^1/_2\, sBdx$ goes to the right and $^1/_2\, sBdx$ to the left. The layer also radiates energy in both directions, amounting to $\varkappa E dx$, if E represents the emission power of the black body within the chosen limit of wave lengths and at the temperature of the layer.

Collecting these effects, one obtains the equations

$$\frac{dA}{dx} = \varkappa\,(E - A) + \frac{1}{2}\,s\,(B - A)$$

$$\frac{dB}{dx} = \varkappa\,(B - E) + \frac{1}{2}\,s\,(B - A) \quad . \quad . \quad . \quad . \quad . \quad (13)$$

If now the temperature and the composition of the atmosphere are supposed to be everywhere the same, so that E, $\varkappa$, and s may be considered as constants, A and B can be solved as functions of x.

Let x be reckoned positive toward the right, and the origin of coördinates taken in the outer surface of the medium, then we shall find *the emergent radiation* R equal to the value which A takes for $x = o$, while at the same time we have $B = o$ Another condition is, that for $x = -l$, we have $A = $ S.

Performing the calculations, SCHUSTER obtains

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[1]) I am using here SCHUSTER's notation, and therefore must draw the reader's attention to the fact, that the above coefficient $\varkappa$ is not quite the same as that occurring in § 2, § 3 and § 4, but corresponds to the expression $\frac{4\pi}{\lambda} \cdot n\varkappa$ of formula (12).

$$\mathrm{R}=2\alpha\,\frac{[(1+\alpha)e^{\alpha(\varkappa+s)t}+(1-\alpha)e^{-\alpha(\varkappa+s)t}]\,E+2(\mathrm{S}-E)}{(1+\alpha)^2e^{\alpha(\varkappa+s)t}-(1-\alpha)^2e^{-\alpha(\varkappa+s)t}}\quad .\quad .\quad (14)$$

where α means $\sqrt{\dfrac{\varkappa}{\varkappa+2s}}$.

In order to study the nature of this rather intricate relation, SCHUSTER assigned a number of different values to the ratio $\dfrac{\varkappa}{s}=\beta$ and to the product $s\,.\,t$, and constructed several diagrams in which the corresponding values of $\dfrac{\mathrm{R}}{\mathrm{S}}$ and $\dfrac{E}{\mathrm{S}}$ were taken as ordinates and abscissae respectively.

As to these results, and a great many other interesting conclusions, we refer to the original paper.

SCHUSTER made no special assumptions connecting $\varkappa$ and s with frequencies.

It lies in our line to bring the selective character of these coefficients to the front. The simple relation to which (14) may be reduced for waves suffering no absorption at all, will prove very important and useful in this connection. Denoting by R_0 the value which R assumes for $\varkappa=0$, we obtain [1])

$$\mathrm{R}_0=\frac{2}{2+s\,.\,t}\,\mathrm{S}\quad .\ .\ .\ .\ .\ .\ .\ .\quad (15)$$

Let us call to mind, before applying this formula, that in deducing (14) SCHUSTER supposed the temperature and the composition of the mass of gas to be uniform, and the intensity of the radiation not to depend on the angle between any direction considered and the normal to the radiating surface. These conditions evidently not being satisfied in the atmospheres of celestial bodies, (14) and (15) only give a first approximation; the influence of the said circumstances will afterwards have to be separately discussed.

In § 4 we introduced the hypothesis that the first term of the damping parameter vanishes at a short distance from the proper frequencies, which means that the region of real absorption is confined to the middle-part of each dark line in all cases, where the conditions are such as to make scattering effects appreciable. On that score we assume the equation (15) to hold good for the rest of the spectrum, including — in the case of the solar spectrum — the outer parts of the Fraunhofer lines.

Equation (15) shows that, with increasing thickness t of the

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[1]) SCHUSTER, l.c. p. 6.

scattering layer, the intensity of the emergent radiation diminishes, but at a slower rate than it would do if scattering acted in the same way as absorption. Putting for instance, $s \, . \, t = 98$, we obtain $R_0 = 0.02 \, S$; and then doubling the layer, we find $R_0 = 0{,}01 \, S$; while, if in the original layer an equal loss of 98 percent had been caused by *absorption*, the layer of double thickness would only have transmitted 0.0004 S.

In a vast mass of gas, like the solar atmosphere, even an exceedingly small absorption-coefficient would suffice to produce a very sensible attenuation of the light. We therefore think it much easier to understand the narrowness of most of the Fraunhofer lines, and their appearance in general, if we assume the absorption coefficient to vanish at a very short distance from the middle of each line, so that in the rest of the spectrum the distribution of the light only depends on scattering [1]) and other influences (refraction, diffraction, etc.).

Our confidence in the validity of the hypothesis is, however, chiefly based on the fact, that it enables one to explain concisely and in mutual coherence a great many astrophysical phenomena, e.g. the systematic displacements of the Fraunhofer lines, and, if also refraction effects are considered, several irregularities in the behaviour of the lines, together with many particulars revealed by the spectroheliograph.

Let us now substitute the value of the scattering coefficient as given by (10) into the equation (15); it thus becomes

$$R_0 = \frac{3\lambda^4}{3\lambda^4 + 16\pi^3 \angle f t . R^2} S.$$

We wish to investigate how R_0 varies with λ. If however, we only consider a small part of the spectrum at once, comprising no more than a few Ångström units, we are free to treat λ^4 and S as constants, and may write

$$R_0 = \frac{a}{a + b R^2} S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

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[1]) The question may arise whether there are perhaps indications from which one might obtain some idea about the magnitude of scattering effects, reasonably to be expected in a gaseous medium of the dimensions of the solar atmosphere. Now, according to RAYLEIGH's theory, the average sunlight loses about 5 % of its intensity by molecular scattering in passing through our terrestrial atmosphere. Substituting $R_0 = 0{,}95 \, S$ in our formula (15), we find $s.t = 0{,}1$. If we make the very rough estimate, that the solar atmosphere is 50 times as thick as the atmosphere of the earth, and has the same average density, we must write for the sun: $s.t = 5$, and, consequently, $R_0 = \frac{2}{7} \, S$. This is not an unreasonable result. It proves that even with a much smaller density the solar atmosphere would be able to produce sensible scattering effects, especially near absorption lines.

The constant b is proportional to the density of the medium, to the thickness of the layer, and to the average mass per scattering particle. The greater each of these quantities is, the smaller will be the intensity of the emergent light (for any value of λ). The only quantity strongly variable with λ in the small spectral region considered, is the factor R^2, in case there is an absorption line.

The upper part of fig. 4 represents $R = \frac{n-1}{\Delta}$ as a function of λ 1). The origin of co-ordinates corresponds to the wave-length λ_0 of a free vibration; the line $P_1\,P_2$, having the approximately constant ordinate $\frac{n_0-1}{\Delta}$, would be the dispersion curve if there were no absorption line at λ_0.

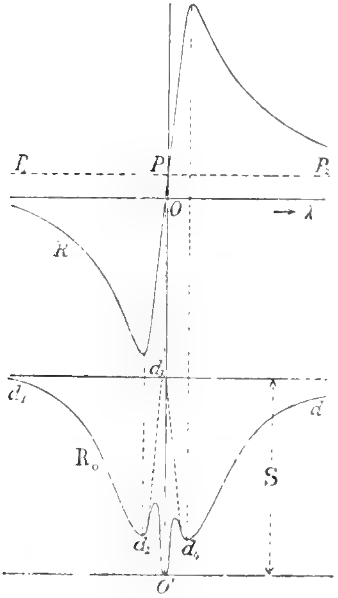

Fig. 4.

Supposing t to be sufficiently great, and R not too small, we may, in the denominator of (16), neglect a in comparison with bR^2; so R_0 is about inversely proportional to R^2. The light is therefore more weakened by scattering on the red side than on the violet side of the absorption lines, if (as supposed in the figure) we have $n_0 > 1$. With *very* strong lines this difference will, however, partly be neutralized, because, according to § 3, the minimum of the refractive index sinks further below n_0 than the maximum rises above n_0.

Taking this into consideration, and preliminarily fixing our attention on the effect of scattering only, leaving that of absorption aside, we may represent the intensity of the emergent light by a curve of the shape $d_1\ d_2\ d_3\ d_4\ d_5$ (fig. 4, lower part). The top d_3 (corresponding to $R = 0$) does not coincide with λ_0, but is a little displaced toward the violet. If, therefore, one would imagine the region between d_2 and d_4, where the loss of light due to scattering passes through a minimum, to be an "emission line", one would have to assign to it a smaller wave-length than to the absorption

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1) In this figure λ increases from the left toward the right; the succession of the kinds of light is therefore opposite to that in the figures 1 and 2, where the frequencies ν were chosen as abscissae.

line, and, applying DOPPLER's principle, would conclude that the radiating vapour moves toward the observer.

Properly speaking, we are not allowed to apply the formulae (15) and (16) to all waves between d_2 and d_4, for where $\varkappa$ is not equal to zero, equation (14) should be used. Let us suppose that only in the middle part of that region $\varkappa$ has appreciable values; then we probably shall obtain a fairly true intensity curve, when subtracting the ordinates of an absorption curve (supposed to be symmetrical with respect to OO') from the ordinates of the displaced, unsymmetrical curve $d_2\ d_3\ d_4$. The result is a sharp drop in the intensity curve, representing a narrow dark line in the spectrum, whose "centre of gravity" is somewhat displaced toward greater wave-lengths (with respect to λ_0), and which is partly caused by absorption, partly by scattering. If one should mistake this line for a mere absorption line, its displacement toward the red would make one think, that the absorbing vapour recedes from the observer.[1])

The above particulars which, according to our theory, the distribution of the light in a wide dispersion band must show, bear a striking resemblance to the phenomena really observed by CHARLES E. ST. JOHN[2]) in the calcium lines H and K of the solar spectrum. And if, besides the consequences of anomalous scattering, we also consider those of anomalous refraction (not noticed in this paper), the agreement between the results of theory and of observation proves to extend to almost every detail of the phenomena described by ST. JOHN. So it is possible to explain the rather intricate pecularities exhibited by the components H_1, H_2, H_3, K_1, K_2, K_3 of the well-known broad calcium lines in the spectrum of the various parts of the solar disk, *without* having to admit with ST. JOHN, that there is a general radial circulation of the calcium vapour going on in the solar atmosphere, with velocities that would amount to 1,97 kilometer per second in the mean for the ascending, and to 1,14 kilometer per second in the mean for the descending motion. I must refer the fuller discussion of these interesting observations to a subsequent paper.

With most lines of the solar spectrum the total region of the dispersion anomaly, from d_1 to d_5, is so narrow, that the particulars concerning the part included between d_2 and d_4 escape our observation. What then remains visible, is only the *asymmetry* of the

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[1]) In a former communication (Proc. Roy. Acad. Amst. XIII, p. 10; Astroph. Journ. **31**, p 428, 1910) I wrote that the central part of the K-line, the true absorption line, cannot be displaced by anomalous dispersion. I did not yet realize, at that time, that even the central line might be an impure absorption line.

[2]) CHARLES E. ST. JOHN, The general circulation of the mean and high-level calcium vapor in the solar atmosphere. Astrophysical Journ. **32**, p. 38—82 (1910).

dispersion bands enveloping the absorption lines. How the systematic displacements of the Fraunhofer lines toward the red, the obliquity of the lines in the spectra of sun-spots, and some other phenomena, may be explained from this point of view, has been shown in former publications [1]).

Anatomy. — "*Notes on the trochlear and oculomotor nuclei and the trochlear root in the lower vertebrates*". By Dr. W. G. Huet. (Communicated by Prof. L. Bolk).

(Communicated in the meeting of January 28, 1911).

In the course of the past year I made several observations regarding the oculomotor and trochlear nuclei and their roots, in Petromyzon, Lophius, Gadus, Hippoglossus, Rhombus, Pleuronectes, Selache maxima and Scyllium Canicula. The results of my researches can be best demonstrated by comparing the relations of the said nuclei in Petromyzon, Selache, and Lophius.

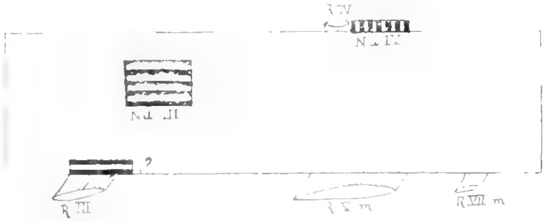

Fig. 1. Petromyzon.

Fig. 1 shows the topographic relation of the oculomotor nucleus and root, the trochlear nucleus and root and the motor V and VII root in Petromyzon.

As will be seen from this figure, the oculomotor nucleus in this animal lies partly on the level of its root-entrance, partly behind. The principal nucleus (Fig. 7), the only III nucleus according to some investigators, lies with its dorsal edge not far from the aquaeduct. Whether the so-called "ventral III nucleus" be a III nucleus or not, I will not state positively. Its topography speaks strongly for this view, as can be seen in Figs. 1 and 6. The cell-type is, however, somewhat smaller than that of the dorsal nucleus. I have not been able to obtain sufficient certainty about the course of its axis-cylinders to enable me to decide this question. [2])

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[1]) Proc. Roy. Acad. Amsterdam, XII, p. 266 and 466 (1909); XIII, p. 2 (1910); Les raies de Fraunhofer et la dispersion anomale de la lumière. Le Radium, t. VII Oct. 1910.

[2]) This cellgroup is regarded by Ahlborn, Johnston, and Schilling as being a part of the III nucleus, but by Tretjakoff, on the other hand, as a cell group independent of the oculomotor.

In the trochlear nucleus it is conspicuous that this lies very dorsally, *above* the aquaeduct in the velum (Fig. 8), as has been described by Schilling [1]) and observed by Tretjakoff [2]) in Ammocoetes.

The further topography of this nucleus shows that it lies nearer the trigeminus root and closer to the trigeminus nucleus than to the nucleus of the III nerve. Moreover the trochlear nucleus lies *in toto behind* its root-end (Fig. 1 and Tretjakoff l. c.).

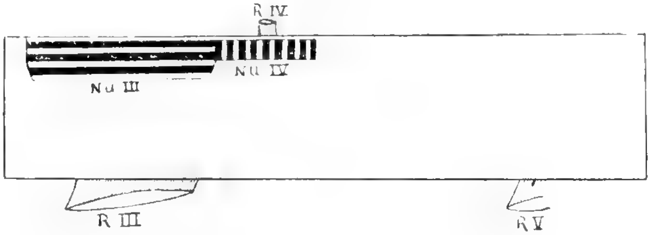

Fig. 2. Selache.

If we compare these relations with Fig. 2, which represents the topographic relations in Selache, we immediately find a difference in the position of the oculomotor nucleus, for the nucleus lies considerably farther frontally than in Petromyzon and surpasses the frontal boundary of its root (see also Scyllium, fig. 9). A ventral III nucleus does not appear here, all the cells lie in the upper third part of the mid-brain basis (fig. 10). Still greater are the topographical differences shown by the trochlear-nucleus and its root in comparison with Petromyzon. The trochlear nucleus no more lies *dorsally* from the aquaeduct *in* the velum, but to the side of the aquaeduct, practically under it, (fig 2). The nucleus is larger than in Petromyzon. A part of it still lies behind the root-entrance, another, much larger part lies in front. [3])

The distance from the IVth nucleus to the V root is greatly enlarged, and the shifting towards the III root is so pronounced that the III and IV nuclei partly overlap each other or pass into each other (Figs 2 and 9).

[1]) Schilling: Das Gehirn von Petromyzon fluviatilis. Abhandl. der Senckenbergischen Naturforschenden Gesellschaft, vol. 30 p. 441 1907.

[2]) Tretjakoff: Das Centralnervensystem von Ammocoetes. II. Das Gehirn. Archiv. f. Mikrosk. Anatomie vol. 74 p. 713 1909.

[3]) The topography of the IVth root and nucleus is not the same in all Selachii. Here I take Selache as object of demonstration because it seems more fit for comparison than Scyllium. Moreover our preparations of Scyllium did not allow us to fix the limits with so much certainty as those of Selache. (Added in the English translation).

I wish here to say that the great distance between IV nucleus and quintus-root is not to be attributed solely to the frontal shifting of the former nucleus. The isthmus in the Selachian is much more extended than in the more compressed brain of Petromyzon [1]) and likewise more than in the Teleosts. That, however, a considerable frontal shifting of the trochlear-nucleus has taken place is also apparent from the facts that a great part of the nucleus now lies in front of its root-entrance, and that the III and IV nuclei overlap each other for a part, while in Petromyzon there was a large gap between them.

Thus we find in these Selachii a strong frontal shifting of the IV nucleus as compared with Petromyzon.

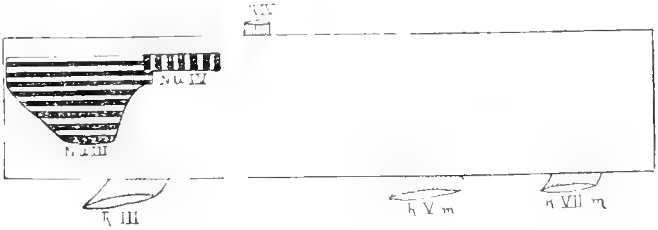

Fig. 3. Lophius.

Passing on to the relation in Teleosts, I refer to Fig. 3, in which the topographic relations of Lophius are given. Here in the oculomotor nucleus a great difference is noticeable as compared with Selache owing to a part of the III nucleus having undergone a strongly ventral shifting (Figs. 3, 11, and 12).

This ventral shifting should not surprise us, for it is known that the abducens nucleus in these animals also occupies a ventral position. It is highly probable that here too, the strong development of the ventral tecto-bulbar (optic) reflex tract is the cause of this displacement which, for the decussated reflexes also, may perhaps find support in the fact that the place of the lowest point of the nucleus agrees with the ventral decussation level of the above-mentioned reflex-tract, which lies (as we know from DE LANGE's [3]) researches) principally *before*, partly on the level of the III root entrance and

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[1]) The compressing of the Petromyzon-brain is also conspicuous in the fore-brain to which SCOTT has already referred. (Journal of Morphologie Vol. I, p. 253).

[2]) KAPPERS. The migrations of the V, VI, and VII nuclei etc. Verhand. der Kon. Akad. v. Wetensch. Vol. 16, 2de Sectie.

[3]) DE LANGE. The descending tracts of the corpora quadrigemina. Folia Neurobiologica. Vol. III, p. 641.

there sends out a series of fibres to the III nucleus (compare also EDINGER and WALLENBERG [1])).

In connection with the more frontal migration of the dorsal nucleus which was found in all Teleosts, I may recall here the fact that DE LANGE found the decussation of the dorsal tecto-bulbar fibres also more frontal than the decussation of the ventral set.

Regarding the III root I will mention that a great number of decussating fibres originate from the posterior part of the III nucleus bordering on the trochlear nucleus, which is interesting in connection with the fact that the IV fibres have also a decussating character.

The trochlear nucleus shows us a further stadium in the process already indicated in the shark, viz. the frontal shifting of its cells which here lie entirely in front of their root-entrance. Although this may partly result from a backward displacement of the root in some Teleosts, a more frontal shifting of the IV cells is also very probable, as is seen from the fact that the IV nucleus in Lophius has also a more frontal position in regard to the III root and V root and therefore, with regard to these points also, the shifting of the IV nucleus can be affirmed, equally in all Teleosts. (Figs. 3 and 11).

The position, which the IV nucleus occupies with respect to its root-entrance in the bony fishes is strongly suggestive of that in human beings (cf. MARBURG [2]) where the nucleus also lies entirely frontad thereof. It has been found by VAN VALKENBURG [3]) that this secondarily produced relation is sometimes shown by a *caudal* remnant of the IV nucleus, which he designates "*nucl. IV posterior*" (cf. JACOBSOHN[4]).

With regard to the trochlear-root the following point may be mentioned.

Earlier investigators had already observed that the trochlear-root traverses the brain-stem with 2 roots (Salmo, HALLER [5]) Gadus, KAPPERS [6])) in some bony-fishes in contrast to other bony-fishes (e. g.

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[1]) Vorlesungen 7te Auflage. — Beiträge zur Kenntnis des Gehirns der Teleostier und Selachier. Anat. Anzeiger, Vol. 31, P. 369.

[2]) MARBURG, Mikroskopisch-topographischer Atlas des menschlichen Zentralnervensystems.

[3]) C. T. VAN VALKENBURG: These Proc. June 25, 1910.

[4]) JACOBSOHN, Verhandl. Preuss. Akad. 1909.

[5]) HALLER. Vom Bau des Wirbeltier-gehirnes. Morphologisches Jahrbuch Bnd. 26, 1898, p. 508. I cannot affirm however HALLER's statement that a part of the IV root originates from the Purkinje-cells of the cerebellum. Nor did I see a "kontinuierliche Zusammenhang dieses Kernes (IV) mit dem rostralwärtigen Ende des oberen motorischen Trigeminuskernes" (l. c. p. 505).

[6]) KAPPERS. The structure of the Teleostean and Selachian brain. Journal of Comparative Neurology. Vol. XVI, 1906, p. 62.

Lophius). The exact course of both these roots was, however, never clear before.

As I had at my disposal some frontal and horizontal series of Gadus and other fishes, I was able to trace the whole system with fairly great exactness and arrived at the following conclusion.

In Lophius piscatorius the decussation of the trochlear root-fibres takes place in a fairly simple way. After their origin in the trochlear nucleus, the fibres pass in the form of one compact bundle closely round the aquaeduct upwards, and cross *in toto* on one and the same vertical level, the decussation occupying about 6 sections of $25\ \mu$, but not more: a difference can only be observed between the fibres mutually in so far as some decussate closer to the aquaeduct, others closer to the surface of the velum, a few even after the exit (somewhat as in Scheme *b* fig. 4).

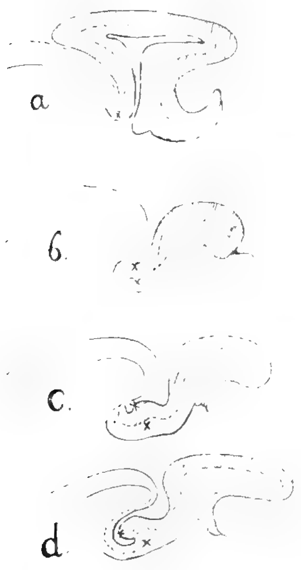

Fig. 4.

In Hippoglossus this relation is rather more complicated, owing to some of the fibres following a pathway separated from the others. Before proceeding to decussation, these fibres (about half of the total number) pass frontally into the valvula cerebelli; then only do they decussate and after the decussation they turn laterally, run again caudally between the valvula cerebelli and its connection with the tectum, to appear at the height of the original velum out of the groove between mesencephalon and cerebellum simultaneously with the other root-bundle which has decussated on the original level (somewhat as in Scheme *c*, fig. 4).

The impression is conveyed as if the anterior part of the trochlear-root and its decussation were drawn frontally by the growth of the valvula into the optic ventricle under fixation of the point of exit.

This dislocation is the most conspicuous in the case of the anterior root-half in Gadus, where the valvula protrudes somewhat farther forward under the tectum (cf. Scheme *d* fig. 12).

Besides by the peculiar dispersion of decussations, the anterior part of the IV root of this animal is also distinguished from the posterior by the fact that it does not run directly round the aquaeduct medially from the tr. cerebello-mesencephalicus, but runs outside that tract (Fig. 11) as has also been observed by Kappers (l. c. p. 62).

That the frontal shifting of a part of the decussation is caused by the frontal growth of the valvula is clear. It does not occur in animals without valvula (e. g. sharks), and in Lophius, where the

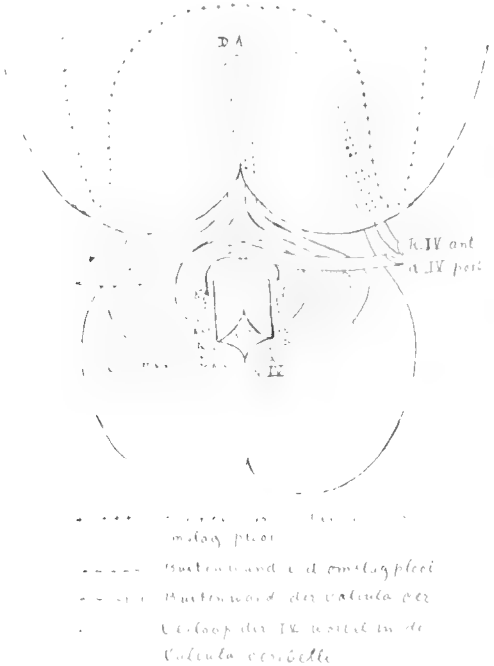

Fig. 5. Gadus.

valvula cerebelli is extremely small, there is neither any question of a frontal shifting of a part of the trochlear fibres. Nevertheless the conditions in this animal furnish us with the explanation.

The diagrams given here show how the said root dispersion is to be deduced from the simple position. In type *a* (shark) the decussation of the fibres occupies but a small space. As the velum is very thin there is only one decussation. In *b* the velum is considerably thickened, principally by the growth of the molecular and Purkinje layer over it. (Type Lophius).

Although the decussation remains on one vertical level, a distinction can nevertheless be made between the fibres which decussate close to the aquaeduct, and those which decussate more or entirely on the surface of the molecular layer.

In *c* the molecular and Purkinje-layer has grown still considerably further under the tectum opticum and exhibits more folds; a consequence of this is the enlargement of the distance between the fibres with a more peripheral and with a more central decussation, which attains its maximum in *d*, practically agreeing with the conditions as shown in Gadus.

This diagram, at the same time, demonstrates clearly that the space in which the frontal root decussates and runs back in a caudal direction, does not lie *in* the cerebellum but between the valvula and the fold connecting it with the tectum.

Summing up my results, I can state the following:

Oculomotor nucleus.

The III nucleus in the lower vertebrates occupies a more constant place in the longitudinal-axis of the brain than IV nucleus. Nevertheless it certainly undergoes a distinct frontal shifting. In a dorsoventral direction the oculomotor nucleus of the Teleosts undergoes a considerable displacement, which agrees with the ventral displacement of the abducens nucleus in these animals.

Trochlear nucleus and root.

The trochlear nucleus in the lower vertebrates exhibits still greater differences in its position with regard to the longitudinal-axis of the brain. In Petromyzon it lies at a great distance behind the III nucleus even behind its own root-entrance, on the level of the trigeminus root-entrance, as has also been proved by TRETJAKOFF for Ammocoetes.

Moreover it lies more dorsally, above the aquaeduct in the velum.

In the Selachii the nucleus lies at a great distance from the trigeminus root and close to the III nucleus, passing into the latter. In Selache it extends partly behind, though for the greater part in front of the IV root-entrance. Moreover, it has come to lie under the aquaeduct. In Teleosts the frontal shifting has reached its maximum. The nucleus lies entirely in front of the IV root-entrance.

In some Teleosts the trochlear root undergoes a peculiar spreading in bundles, e. g. Gadidae and Pleuronectidae, owing firstly to the root being split into two parts before decussation by the passing through of the tr. cerebello-mésencephalicus; secondly, the part which runs round outside that bundle is drawn forward by the frontal growth of the velum that grows out to valvula cerebelli, in consequence of which it decussates more frontally, and then again runs caudally between valvula and its connection with the tectum.

This severing of the decussation levels also explains the splitting of the trochlear root into two roots at the exit, which until now has not been found in fishes without valvula (sharks) nor in those bony fishes where the valvula is very small (Lophius).

Bacteriology. — "*Acetifying air- and ricebacteria the cause of Polyneuritis gallinarum*". By J. H. F. Kohlbrugge. (Communicated by Prof. C. H. H. Spronck).

(Communicated in the meeting of Januari 28, 1911).

The above title is at the same time a hypothesis which I intend to prove in the following pages.

It is a fact generally known and acknowledged that the discovery of Polyneuritis gallinarum by Eijkman, classified the so mysterious Beri-Beri in general with those phenomena that can be elucidated by experimental investigation. That Polyneuritis gallinarum belongs to the same group of diseases that includes human Beri-beri was likewise acknowledged by nearly all investigators; consequently experiments with poultry were made in order to learn how to fight the human disease.

By following the way taken by Eijkman, many investigators have brought to light a great number of facts, and yet the causa movens of the disease continued to be as mysterious as before, whosoever supposed that he had discovered it, might be sure that a subsequent investigator would declare it to be harmless.

In 1901 I was experimenting in Prof. Eijkman's laboratory about the autosterilization of the small intestine, and, as Eijkman was at the same time engaged in experiments regarding Beri-beri, this induced me, in order to study the intestine-flora of chickens, to examine, for economy's sake, the intestines of those chickens thad had died of Polyneuritis gallinarum. As I examined however likewise some chickens that had been killed, I soon remarked that the intestine-flora and the intestine-sapreaction of these two groups of animals showed very apparent differences. Since that time I became convinced that the Beri-beriproblem should be studied from the intestines of poultry. Several investigators indeed have pointed out that presumably Beri-beri is caused by poisons formed, during digestion, by micro-organisms in the intestinal canal [1]). It was however astonishing that nobody consequently chose the intestines and their flora as point of issue, and that, if this was occasionally done (Dubruel, Wright it had no result whatever.

On account of my return to Java I could not continue my investigations, but constantly, there and afterwards in Europe, I harboured the design of applying this method of investigation. Not

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[1]) Eijkman, Laoh, Maurer, Wright, Herzog, Jeanselme, Van Gorkom.

before Oct. 1910 I could accomplish this design, when Prof. SPRONCK was kind enough to place at my disposal a room provided with all that was indispensable for such an investigation, to be used as a laboratory. I set high value on the fact that I may add to this that Prof. SPRONCK is quite willing to declare that the nature and course of my investigations remained entirely unknown to him.

In order to examine chickens suffering from Polyneuritis gallinarum I had first to make healthy chickens ill, and succeeded in doing so, according to the method taught by EIJKMAN i. e. by compulsory feeding with white entirely prepared rice.[1]) After 18 or 19 days every chicken thus fed became ill, showing the wellknown symptoms of Polyneuritis gallinarum. [2])

During these experiments I observed in the first place that during November and the first half of December the rice, neutral after sterilization,[3]) grew sour within a few hours when it was exposed to the air. The first thing I wanted to know now was: Why does rice acetify? [4]) Nobody could give an answer to this question, not even Prof. BEYERINCK of Delft, who kindly listened to my questions but felt even inclined to doubt the fact; I myself could however doubt no longer, for I saw that rice kept, after the sterilization, in well shut vessels remained neutral, whilst I saw it turn sour when it was exposed to the air in the different rooms of this new laboratory, where never before experiments concerning fermentation had been made. The rice turned also sour in the crop and in the intestines of chickens. From the above it appears that the rice did not turn sour by a simple chemical process. Consequently the rice must turn sour either by bacteria of the intestines or by bacteria of the air, or by both. By a series of experiments the obligate bacteria of the intestines of chickens were soon excluded, consequently had the acetification to be explained by the bacteria of the air. Now I made my investigations in that direction, but it was anything but easy to

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[1]) In order to exclude however any idea of spoiled rice, the rice was sterilized at 120° before it was used. By so doing I obtained likewise a greater conformity with the often sterilized articles of food on board sailing-vessels that are so often accused of being operators of Beri-beri

[2]) Frequent thin defecation, emaciation, paralysis, cyanose, dyspnoe (EIJKMAN).

[3]) Uncooked not sterilized rice has always a feebly acid reaction.

[4]) As sour fermentation was then for me only a sound to which I could not attach any idea, I applied in the first place to the vinegar-works "de Roos" at Amsterdam, where Mr. O. WINFORTH in the kindest way furnished me with information and placed at my disposal the literature about vinegar fabrication; Mr. H. VLAANDEREN, a well known dealer in groats here, informed me about the different sorts of rice, the way of preserving rice etc. etc. To both my sincerest thanks.

isolate these micro-organisms that acetify rice among the mixture of moulds, fungi, and bacteria that fall out of the air on wet sterilized rice [1]). This micro-organism however was found after all. It is a small, short rod, having great resemblance to the Colibacillus of the intestines. The isolation was rendered still more difficult because this little rod is very polymorph, and because a special medium and special breedingtemperature are required to obtain a good result.[2])

This bacillus acetifies within 24 hours neutral sterilized rice, which but for this bacillus always remains neutral.

Just now I have compared it to Colibacillus, on the other hand it reminds me of the vinegar bacilli by its polymorphy. The more so, because it possesses the peculiarity, demonstrated by BEIJERINCK in some vinegar bacteria, of showing on some special media easily deviating and hereditary qualities. So e. g. it is not difficult to deprive it of its power of exciting fermentation. According to BEIJERINCK there are also vinegar-bacteria that do no longer acetify, and must have originated in acetifying ones. Only on fit media, and when cultivated at the required temperature, and constantly having a new opportunity of acetifying rice, it is kept in good condition. It cannot be kept in rice, as it soon dies in the acid it has produced itself. Grow and multiply the bacillus does on the other hand on every medium that is not too sour, even though it afterwards dies or modifies itself in many of them. After domestication it accommodates itself to altered circumstances as to a feeding that was first refused or to a temperature at which in the beginning it was killed. Consequently we have here an exceedingly resisting bacillus, which could be cultivated in November and December in the whole laboratory. When however in December the temperature reached

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[1]) At the present moment this is not difficult, since I found out that moulds and fungi only multiply on rice, when the rice has obtained an acid reaction by the bacterium causing rice to turn sour. Consequently the moment when the rice that is at first neutral, begins to show a feeble acid reaction, must be carefully observed, then, in most cases, pure cultures of the bacillus acetifying rice will be obtained by inoculation on specially prepared ferment. This is still easier in winter when the air of the room that has grown perfectly dry by the heat of a stove so that scarcely any moulds and fungi are found in it.

[2]) The first inoculation from sour rice very often had not the desired result on the common alkalic or acid media at 37°C., very often they do grow, but lose their power of fermentation. Rice which is in the first place indicated as a medium cannot be made into a transparent medium. On ferment and malt the best results are obtained at a temperature of 17—23° C. On ferment results are obtained to a temperature as high as 40°, on malt not. I owe the prescription for malt to Prof. BEIJERINCK, the recipe for ferments was used and accidentally tried in this laboratory. Only on rice, glucose and malt acid is formed.

occasionally and even repeatedly the freezing point, the bacillus disappeared almost from the air. It became so rare that cooked white rice could be exposed from 5 to 6 days to the air without turning sour[1]). Did it do so in the end, then the same short rods were always isolated from the rice.

On account of its polymorphy, and soon diminishing efficacy on artificial media, it was however desirable for me to dispose of a source from which every day new generations could be isolated. In December and January the air no longer produced them. As this bacillus seemed to have a special affinity for rice, the idea occurred to me that it might perhaps be found on dry grains of rice.

For this reason dry grains of rice were sown on sterilized neutral rice and really every grain of rice[2]) proved to be a source of acid, in which the above mentioned bacillus was found. It seemed strange that this bacillus can live in such a perfectly dry grain. Therefore one might have surmised that it sticks perhaps only accidentally on it, as an air-bacillus. Further the finding of bacteria on or in all fully prepared grains of rice reminded too much of those investigators (VAN DIEREN etc.) who attribute all sorts of evil consequences especially Beri-beri to feeding with long kept, peeled grains. Both considerations induced me to examine unpeeled rice (gaba) in the following way. In order to exclude all air-bacteria every grain of rice (gaba) was separately passed several times through the gas-flame, then the coarse yellow skin, and the fine white one under it is charred, and only the interior part of the grain remains white. The grains are now ground in a sterilized mortar, and this mixture of carbon and white amylum is inoculated on neutral sterilized rice. Then it appears that the acetifying bacillus lives likewise inside the unpeeled grain of rice, and continues to live, when the rice is treated in the way we have just described, for the neutral rice grows sour, and the bacillus appears.[3])

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[1]) If this investigation had begun as late as December, I should never have observed the acetification of the rice, and consequently never have obtained the results I have come to now. Until now I have not yet been able to capture the bacillus from the open air, and it is by no means impossible that it is more correct to regard it as a wall-bacillus living inside the houses on the walls and spreading itself thence into the rooms.

[2]) Common rice, white not glossy rice of Java, Moulmein, Rangoen and Bassein harbours this rice-bacillus, the latter more than the other, or a more vigorous variety than the other sorts.

[3]) It is an interesting problem, when this bacillus enters into the rice, whether in the fields, or after it has been taken to the barn This question must be solved in India or Italy. Perhaps rice cannot ripen without bacteria. What part do these bacteria act? These might be questions of as great agricultural interest as the

I followed the course of my own investigations by indicating only one bacillus, this is however less exact. Accidentally the before-mentioned short rod had first drawn my attention, and as every bacteriologist is anxious to work with pure cultures, it was everywhere isolated, in doing which I was often hindered by a certain lengthened rod that made its appearance in the cultures, for which reason several cultures were disapproved of. It appeared afterwards that in every portion of acetified rice and in every dry grain of rice both bacilli are found, which both make rice sour; it seems consequently that they live as in symbiosis, or support each other. Since that time I often worked with this mixture, indicated by nature, which appears to have a much greater vital strength [1]).

If one keeps the rice of the noon-table in India till evening it may easily have turned sour, which proves that these bacilli acetifying rice occur likewise in the tropical regions; an investigation ought to be made whether their appearance is likewise subject to season or the state of the weather [2]).

I should like to communicate here what acid was formed by this fermentation. Dr. STAAL was kind enough to offer me to isolate and determine the acid; this investigation however is not yet finished.[3]) I have likewise to thank Dr. STAAL for the information that in order to neutralize the acid produced by bacilli from 20 grams of dry grains of rice in 7 days 24.6 cub. cm. $\frac{n}{10}$ NaOH was required.

This investigation into the fermentation of rice was consequently finished, and relying on the reports of EYKMAN and others that rice turns sour in the crop of chickens, I passed over to the following working-hypothesis. The acetifying agens in the crop and intestines

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well-known nitrogen-binding-bacteria for the roots of leguminousplants (BEIJERINCK). As Beri-beri does not occur in Suriname, I shall try to obtain rice from that colony for examination.

[1]) Now the question occurs to me, if not many of the unsuccessful results I obtained with media and breeding temperatures are to be attributed to my cultivating only with the short rod. Or are they after all two growing forms of the same bacillus? The vinegar-maker Mr. WIXFORTH told me that for his products he thinks pure cultures unfit.

[2]) A rice-acetifying-bacillus was isolated by MAURER (Medan). I am convinced that his bacterium A, is closely connected to, if not identical with the one I isolated at Utrecht. MAURER's culture perished alas! I shall repeat the experiments described by MAURER in order to ascertain how far the conformity goes. ROST seems likewise to have found a similar bacillus in 1910.

[3]) It is no Acidum lacticum (contra EYKMAN) and no Acidum oxalicum (contra MAURER). Nor is it volatile for it does not diminish by sterilization.

of chickens are not the common intestine bacteria, but the air-bacteria, described above, which acetify rice. A series of experiments followed from which appeared 1st. that the obligate intestine bacteria do not acetify rice, 2nd. that in the crop and intestines of chickens that died from Polyneuritis gallinarum the air-bacterium that acetifies rice can be shown; 3rd. that in acute cases of Polyneuritis the air-bacterium can almost supersede the intestine-bacteria.

Another working hypothesis followed. As, by feeding with rice Beri-beri presumptively results both in India and Europe [1]) from poisons developing themselves during the digestion out of food, containing amylum (EYKMAN); as rice has a special affinity for the above-described acetifying air-bacilli, so much so, that they are even found in every dry grain: it may be admitted that these bacilli are the generators of Polyneuritis gallinarum not in the usual infectuous sense, but because they are pernicious to the body, when they turn the rice sour (in the intestines), either by the acid itself or by accessory products. If this supposition is correct, these bacilli must be harmless at subcutaneous injection, but they must cause Polyneuritis gallinarum when they are introduced into the intestines together with the food.

It was soon shown that these bacilli, and even entire cultures together, injected into the breast-muscles and into the peritoneum do not cause Polyneuritis gallinarum [2]). The last and most important experiment remained.

I communicated already above that my chickens fed with sterilized rice, show after 18—19 days the well known symptoms of Polyneuritis gallinarum; [3]) EYKMAN who acted somewhat differently obtained the same result. [4]) If now the bacillus acetifying rice is the generator of the

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[1]) A European Beri-beri epidemy was the one in the RICHMOND-asylum at Dublin. I do not know what food was taken there.

[2]) Nobody will be astonished at the fact that chickens lose their appetite, if for days together 10-12 platina loops of these bacteria are injected into their peritoneum, even physiological salt-solution would make the ill. But they are not attacked by Polyneuritis, and do not die. Afterwards I injected into the breast-muscle which they could stand better.

[3]) The first week they receive grains of rice which are strown into the chicken-house, soon they refuse this food, so that the 6th or 7th day one must proceed to compulsory feeding with sterilized rice-porridge.

[4]) EYKMAN does not sterilize the rice, has the grains only ground and mixed with water, consequently the chickens receive the bacteria living in the grains of rice into their crops, when these are still alive. This is most likely the cause that EYKMAN often obtains stagnation of food in the crops by expansion and fermentation. I never had this result. Has the ground and moistened rice been kept a long time, it might occasion sudden death, as EYKMAN often observed.

disease, chickens fed with sterilized rice, and moreover with cultures of these bacteria, must much sooner be attacked by Polyneuritis gallinarum than the former, as these receive only such bacilli as accidentally pass from the air into the crops;[1]) whereas the latter swallow with the rice entire cultures of these bacteria.

It appeared indeed that chickens, fed with sterilized rice and cultures of acetifying rice-bacilli bred on ferment, showed already on the 3rd day symptoms of paralysis and cyanosis. The third day they are sitting in the cage with paralyzed feet and bristling feathers, blue combs, show soon dyspnoe and die the fifth day. A dreadful diarrhoea was perceptible previously and the animals are enormously emaciated in those five days, so that even the breast-muscles have disappeared. All symptoms correspond entirely to those which chickens, fed with rice only, do not show before 24th or 25th day, but here they coincide in a short space[2]).

This experiment proved undubitably that the air- and rice-bacillus generating sour fermentation, isolated by me, can cause the symptoms of Polyneuritis gallinarum when it is introduced into the intestines of chickens.

The bacteria in question, the froth of the fermentation can be observed post mortem everywhere in the intestinal canal, the bacteria themselves seem sub finem to merge into the blood, and this fact explains that formerly so often bacteria were isolated from the blood of Beri-beri patients and chickens. Perhaps then already the same bacillus was found, which however was always rejected as the morbific agent, because it was supposed that it was to be expected that the morbific agent, when brought into the blood, must cause Beri-beri. It was not yet known that Beri-beri seems to belong to a peculiar group of diseases that find their origin in micro-organisms, and yet are no infectious-diseases in the usual sense of the word, and are best characterized as fermentation-diseases. In these diseases the morbid organism is only detrimental in the intestines and harmless in the blood.[3]). For the present this remains a theoretically construed group, among which I classify Aphthae tropicae[4]), the

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[1]) Or the very bacteria of rice with EYKMAN's method. This is of course never the case with man, as he never eats raw rice. Yet I once saw a fanatical vegetarian do so, and I understand now why he perished from violent diarrhoea.

[2]) By adding fewer bacteria to the rice the process can be rendered slower.

[3]) This is the reason why DE HAAN and GRIJNS searched in vain in the serum of recovered Beri-beri patients, or in the serum and hydropericardial fluid of patients for "complementsbinding." Neither did they find any in chickens.

[4]) According to Dr. MAURER's and my own investigations.

disease of BARLOW and scorbut.[1]) May they not remain long a theoretically construed group. Investigations with regard to scorbut have already been taken in hand. Now we should be anxious to know which fermentation-products generate the symptoms of the disease, this however is the task of the chemist rather than mine. At all events we have in the first place to wait for what STAAL's investigations concerning the acid that is formed, will teach us.

Another series of experiments related to the facts, discovered by my predecessors, that chickens fed either with unpeeled rice or with rice and raw meat, or with rice and Kadjang hidjoe etc. do not become ill at all, or do so later.

When cultivating the acetifying bacteria, it appeared that they develop themselves only in that part of the rice that by cooking separates a pultaceous matter, which we call "starch", and in India tadjen[2]). This starch is analyzed by the bacteria into water, gas, acid and perhaps unknown products. The more starch is formed by cooking, the more luxuriously the bacteria grow in such rice, the less starch, the less food for the bacteria, the less formation of gas and acid.

Even by repeated cooking of rice the grains remain intact, the starch has however separated from them, and makes the grains stick together, and in these intervening spaces of starch one sees the bacteria grow rankly, and change it into water in which at last the grains float.

White fully prepared rice produces much starch, cooked gaba (unpeeled rice) produces hardly any starch, sterilized gaba again produces some more starch. The longer the unpeeled rice is cooked, the more starch is obtained, and consequently it is to be understood that (GRIJNS, MATSUSHITA) padi cannot entirely protect against Beri-beri. If one adds to fully prepared rice ferrihydroxid, eggs[3]), spirits, animal charcoal[4]), fresh meat, much less starch is formed[5]). By

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[1]) NOCHT and HOLST

[2]) To the rice-starch-works of J. DUYVIS I owe the communication that a not unimportant part of the rice cannot be turned to starch, a considerable residue remains which is sold as food for cattle, it contains 87,74 °/₀ of organic matter (STAAL). The percentage of starch of the various kinds of rice is very different.

[3]) MATSUSHITA asserts that the addition of eggs to rice prevents Beri-beri.

[4]) These least.

[5]) Addition of these substances never impedes the growth of the bacteria and the fermentation, though it is inferior on account of the inferior quantity of starch.

anology I conclude that Kadjang hidjoe [1]) will have a similar preventing influence on the formation of starch. [2])

Moreover it is by no means indifferent whether these substances are mixed with the rice before it has been cooked, or after the cooking has taken place. The starch that has been formed already [3]) cannot be precipitated, either the starch that is in process of formation is precipitated, or its development is prevented.

It is very remarkable that the natives, when left to themselves, never cook rice but steam it, whilst the steaming is variegated by washing, the consequence of which must be that the starch disappears, is washed away. Rice for prisoners and soldiers on the contrary is cooked, and though one tries afterwards by evaporation to give to the grains of rice the dry appearance that steamed rice has, yet the starch remains in the food. The first group is consequently guaranteed against Beri-beri, the other exposed to it. The danger augments considerably, if one eats by preference cooked or steamed rice, after it has entirely cooled down. On such rice the acetifying bacteria of the air have fallen down, not only does it smell sour, but it obtains that agreeable flavour reminding of fruit, a consequence of fermentation that is highly praised by gastronomers [4]). Food containing amylum in which few substances are found that form starch guarantees against Beri-beri, and there exists moreover a sort of starch from amylum that ferments, but through which only very little acid is formed. So our bacillus very easily produces water and gaz from starch of potatoflour, but by this process only a very small quantity of acid is formed. Consequently it is not strange that with potato-flour EIJKMAN cannot excite Beri-beri [6]).

A controversy arose between EIJKMAN on the one hand and GRIJNS with HOLST on the other, whether Beri-beri can occur when feeding with sterilized meat. I have not repeated these experiments but I draw the attention to the fact that our bacillus grows vigorously on

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[1]) ROELFSEMA, GRIJNS, HULSHOFF-POL.

[2]) The influence of Kadjang hidjoe and rice-bran may however be quite different, see below.

[3]) For this reason the extract of dedek, or the salts found in dedek added to rice that has already been cooked, will not prevent Beri-beri (GRIJNS contra EIJKMAN).

[4]) Tamil rice on the contrary which protects against Beri-beri stinks (FRASER, STANTON). It is submitted to a treatment by which the starch-substances are lixiviated, by this process the fermentation that gives an agreeable flavour is rendered impossible.

[5]) Sterilized potato-flour ferments somewhat quicker.

[6]) Nor is it strange that neither this flour nor gaba can absolutely protect against Beri-beri (GRIJNS).

sterilized meat, whilst it is quite superfluous to add anything to it [1]).

Instead of feeding-experiments I took fermentation-experiments. Though I acknowledge that these need not cover each other entirely, yet until now they supplied nothing that is contradictory to the facts observed by feeding, so that my experiments perhaps may explain these facts and plead powerfully for the suggestion that Beri-beri rests entirely on fermentation processes [2]).

Moreover I think that it is of the greatest importance that these bacilli are found much more frequently in-doors than out-of-doors, that, in Europe at least, they are restricted to certain seasons, and that very dry air makes them disappear.

This fact explains why Beri-beri is more frequent near the sea-shore (VORDERMAN), with bad ventilation (VORDERMAN), in houses built in the European way (V. D. BURG); that expeditions in woody, marshy regions are notorious for the great number of Beri-beri patients (Djambi). Wherever the local conditions are favourable for the development, a so-called Beri-beri epidemy may break out, or a so-called Beri-beri house or ship may be found. If a house is strongly infected with these bacteria, the tenants can be attacked by Beri-beri from inhalation, from swallowing dryly, from drinking water, though they take their food (rice) outside the building [3]).

As the cultivation on various media and at various-temperatures taught me, how easily varieties may come into existence, and that the fermentation-process is moreover promoted by symbiosis, I suppose that varieties of this bacillus may exist that are extremely malicious. They obtain this quality most likely in the following manner. The bacillus must first accommodate itself to the medium,

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[1]) A thick fleece of bacteria is formed at the surface of the fluid floating on the sterilized juice without acetifying it.

[2]) It is by no means my intention to explain all symptoms, observed by monotonous feeding, by the fermentation excited through the bacillus. The want of nucleopotreides or nucleine (JEBBINK, NOCHT, SCHAUMANN) may either predispose or promote the disease or be in itself the cause of it. This nucleine theory is not attacked by my investigations. A bridge might be built across, if it could be proved that nucleoproteides are analyzed by fermentation. In that case fermentation would not produce active destructive substances, but death would be caused by depriving the body of the required food This theory appears to me very admissible, as up till now, I could not succeed in making chickens sick by intermuscular injection of the pure fermentation fluid.

[3]) So in the building of the doctor-djawaschool at Batavia (1900) 30 % of the pupils who took their meals outside the school became ill. Would perhaps new walls offer a fit medium and this perhaps be the cause that rice turned so quickly sour in this new laboratory? BENTLEY was likewise of opinion, that the generator of Beri beri must be a wall-bacillus.

and the temperature of our intestines, when it has succeeded in this, and leaves our body with the faeces (VAN GORKOM), it will operate much more strongly when it enters into another man's body (WRIGHT). In this way, I think, I can likewise explain why the disease seldom develops itself suddenly, and yet in other cases can assume such an acute form (Djambi). In such extra-ordinary cases it mocks all prophylactic measures, though they may be ever so rational (HULSHOFF POL) [1]).

So far about the aetiology of Beri-beri. A single word more about the therapy. The latter can be divided into prophylactic and causal therapy.

We know already very much about prophylactic therapy. We know that Tamil-rice and red rice usually protect against Beri-beri; we know that a nourishment more in accordance with the European usages suppressed Beri-beri in the navies of the Dutch Indies (VAN LEENT) and of Japan; JEBBINK has likewise shown in his dissertation the great difference there is between the two methods of nourishment. Here I shall only emphasize the fact that the native soldier, who is much more subject to Beri-beri than the European soldier, receives in his food more substances containing amylum than the latter. Moreover we know already, and the investigation lying before us confirms it that for fighting fermentation, the way in which rice is prepared is of great importance. One should always try to apply a method by which the starch is washed away. Further one should examine, if the starchy substances can be removed before the rice is transported to the barn and peeled. Most likely the preparation has much greater influence than the age after complete decortication or the bringing into the barn of fully prepared rice (VAN DIEREN contra EYKMAN and GRIJNS).

Other experiments have taught that the addition of certain substances to the cooked rice prevent the appearance of the disease. LAOH mentions the side-dishes usually taken by the natives, others praise especially kadjang hidjoe (HULSHOFF POL), EIJKMAN rice-bran, SCHAUMANN ferment. When cooked directly with rice these substances

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[1]) Consequently I do not think strange at all that WRIGHT could make monkeys suffer from Beri-beri by feeding them with rice and banana, which had been rubbed on the floor of sick-rooms where Beri-beri patients were nursed, whilst subcutaneous injections remained unsuccessful (HUNTER, KOCH). Transportation of the disease by ships and men to regions that had hitherto been exempt from Beri-beri can be explained, if it may be admitted that rice in those regions did not show the same fermentation phenomena, or that a specially virulent variety had been introduced which had become extremely active on account of its passage through the human body.

might, as mentioned before, prevent the formation of starch, but if I rightly understand the investigators, they did not act in that way: consequently this explanation does not hold good. Moreover they might hinder the growth of the bacilli or prevent fermentation. I know by experiment, that these substances when alcalised do not hinder the bacilli, they prevent the growth however undoubtedly by the acid they contain themselves.

If on the contrary we admit that the symptoms of the disease depend on the fact that the fermentation in the intestines does not produce active poisons but deprives the body from feeding-substances (NOCHT. SCHAUMANN) without which it cannot continue to exist, it would be possible, that these were added again to the body by the beans called kadjang hidjoe etc. This point requires further investigation.

Causal therapy will try to fight the bacilli[1]) and the fermentation and its products in the intestinal canal. In this direction however as yet no experiments have been made with the exception of those with the above mentioned articles of food. Causal therapy can take another road by counteracting the influence of substances that have eventually crept into the blood, or by supplying such substances as may have been withdrawn from it. I know that Prof. EYKMAN is making experiments in that direction.

In view of the observations of my predecessors, of my own investigations and of the fact that, in so far as I have hitherto been able to apprehend, neither the injection of the bacteria, nor that of the filtrate of acetified rice (interperitional or inter-muscular) excites Polyneuritis in chickens, I must admit that the bacilli causing fermentation deprive, from the intestine canal, the body of substances, by which the quick emaciation must be explained. (500 gr. in 4 days) at a slower process the symptoms of paralysis show themselves first, but at all events the withdrawal of these substances ultimately renders life impossible, and death is the consequence[2]).

If really, as now-a-days is generally admitted, human Beri-beri and Polyneuritis gallinarum is to be attributed to the same or akin causes,

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[1]) MAURER thinks he can obtain this by acids (acidum lacticum, muriaticum, phosphoricum). As the bacillus soon dies in acidiferous media, the acid produced by the bacillus itself applied in great abundance might act as a curative.

[2]) In all therapeutical experiments it is strictly required to make with HULSHOFF POLL a sharp distinction between the symptoms proper of Beri-beri and the subsequent consequences, on account of the degenerated nerves. Only against the former we may expect to find an active remedy. Moreover not all that we remark in chickens is applicable to mammals, as HOLST's experiments with rice feeding of Cavyas have shown.

[3]) YAMAGIWA is of opinion that the regressive metamorphosis is a consequence of anaemia.

it must be possible, in case of acute Beri-beri, to isolate such like bacteria from the faeces of the patients. It is however possible that they perish in the rectum, as is the case with Polyneuritis of chickens, in whose whole intestine canal very often the acetifying bacilli are exclusively found, and yet it is very difficult to detect them in the Coecum. Consequently we shall have to wait for a favourable case, in which post mortem a fresh stomach and the small intestines can be examined [1]). Should even under the most favourable conditions (acute death in the first stadium) the bacilli not be found, either human Beri-beri and Polyneuritis gallinarum is not the same, or there are different generators of the many diseases that have been classified with the group Beri-beri. Yet I hope that, even in this case, the results lying before us may be of use to ascertain the aetiology of these diseases, which are, at all events, closely allied to Polyneuritis gallinarum. Though a preliminary communication does not require that the literature of the subject is reproduced in it, yet I have taken account of the literature in order to avoid prejudicing prior rights of others, and to control my own results. Prof. EYKMAN was kind enough to place his collection of separata at my disposal, for which kindness I offer him my sincerest thanks. Much literature is likewise found in the book of DÜRCK.

I foresee that, when my results are controlled, the fact that it is exceedingly difficult to cultivate the bacillus pointed out by me, with conservation of its virulence, will excite the most important criticism. Moreover the bacilli (from air or wall) isolated from sour rice act much stronger than those isolated from rice-grains. Other differences depend on the seasons. Experiments with bacilli that have already been modified will of course give other results. I hope however to succeed in finding a method enabling us always to dispose of vigorous bacilli. The capriciousness or variability of the bacillus reminds us of the fact that likewise the evidence of the symptoms of Beri-beri with rice-feeding is exceedingly capricious, with regard to the earlier or later date of its appearance, as the protocols given by EYKMAN and HOLST show (differences of three weeks). This resistance is attributed to the animals, which may be true but has not been proved.

I give here these preliminary results, as my personal means do not allow me to continue the required experiments with different articles of food, and the different methods of preparing rice in every detail. Perhaps others disposing of ampler means will be inclined to repeat these experiments, and to bring them both here and in India to the end wished for.

Utrecht, 27 January 1911.

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[1]) According to VAN GORKOM, WRIGHT, DUBRUEL human Beri-beri always begins with inflammation of the mucous membrane of the stomach and the intestines.

Physics. — "*A new accurate formula for the computation of the self-inductance of a long coil wound with any number of layers.*"

By F. L. Bergansius (Communicated by Prof. W. H. Julius).

For the accurate computation of the self-inductance of multiple layer coils, different formulae are available in the case the cross section of the coil is a square, a circle or a rectangle. All these formulae only give results of a high degree of accuracy, when the cross section is not too large in comparison with the mean radius, and besides for the rectangular section restriction is made, that the length of the coil shall not considerably surpass this mean radius.

For the case of a *long* coil or solenoïd wound with many layers of wire, to my knowledge no formula has been derived, which, either in a closed form or in the form of a converging series, represents the value of the self-inductance with a high degree of accuracy.

Louis Cohen [1]) has derived for this case an approximate formula of the following form:

$$\left.\begin{aligned}
L = 4\pi^2 n^2 m & \left\{ \frac{2a_0^4 + a_0^2 l^2}{\sqrt{4a_0^2 + l^2}} - \frac{8a_0^3}{\pi} \right\} \\
+ 8\pi^2 n^2 & \Big\{ [(m-1)\,a_1^2 + (m-2)\,a_2^2 + \ldots] \left(\sqrt{a_1^2 + l^2} - \frac{7}{8}\,a_1 \right) + \\
& + \tfrac{1}{2}\,[m\,(m-1)\,a_1^2 + (m-1)\,(m-2)\,a_2^2 + \ldots] \left(\frac{a_1\, \delta a}{\sqrt{a_1^2 + l^2}} - \delta a \right) - \\
& - \tfrac{1}{2}\,[m\,(m-1)\,a_1^2 + (m-2)\,(m-3)\,a_2^2 + \ldots]\, \frac{\delta a}{8} \Big\}
\end{aligned}\right\} \quad (1)$$

wherein a_0 = mean radius of coil $a_1, a_2 \ldots$ = radius of the first, second layer reckoned from the axis of the coil; δa = distance between two consecutive layers; l = length, n = number of windings per cm. m = number of layers.

Cohen says that the results obtained with this formula are accurate to within one half of one percent for a solenoïd, whose length is twice the diameter, the accuracy increasing as the length increases.

Apart from this moderate accuracy, this formula (which, moreover, contains errors in the third and fourth terms) is very laborious for numerical computations, when the number of layers m is large.

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[1]) Louis Cohen, Bulletin of the Bureau of Standards IV, 383.

Edward B. Rosa [1]) describes in the same part of the above mentioned annual, a method for the accurate computation of the self-inductance of a coil of any length wound with any number of layers, which he presumes to be absolutely correct and which is used by him to check the results obtained by other formulae, especially Stefan's. This method, though based on a correct principle, will, if applied in the manner used by Rosa, only then lead to very accurate results, when the total depth of the windings on the coil is *very* small compared with the mean radius.

In the following pages I propose to give the derivation of a new formula, which, in a simple and for numerical computation very convenient form, represents the self-inductance of multiple layer coils with a high degree of accuracy in all cases in which the formulae for short coils fail.

For the mutual inductance between two coaxial cylinders of equal length Maxwell [2]) has derived the following expression:

$$M = 4\pi^2 n^2 a^2 [l - 2A\alpha] \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

wherein

$$\alpha = \frac{l-r+A}{2A} - \frac{a^2}{16A^2}\left(1-\frac{A^3}{r^3}\right) - \frac{a^4}{64A^4}\left(\frac{1}{2}+\frac{2A^5}{r^5}-\frac{5A^7}{2r^7}\right) -$$

$$- \frac{35a^6}{2048A^6}\left(\frac{1}{7}-\frac{8}{7}\frac{A^7}{r^7}+\frac{4A^9}{r^9}-\frac{3A^{11}}{r^{11}}\right) - \quad . \quad (3)$$

$r = \sqrt{A^2+l^2}$, $A =$ radius of outer cylinder, $a =$ radius of inner cylinder, $l =$ length, $n =$ number of windings per cm.

Te last term of α has been added to the derivation by E. B. Rosa [3]).

Generally the self-inductance of a coil is found by integrating the expression for the mutual inductance between two elements of the section twice over the whole area of this section.

In order to obtain this integral we suppose the solenoïd to be formed by a very great number m of layers. Indicating by a_1 the radius of the *outer* layer and by da the distance between two con-

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[1]) Edward B. Rosa, Bull. of the Bur. of St. IV 369.

[2]) Maxwell, Electricity and Magnetism, II, § 678.

[3]) E. B. Rosa and L. Cohen, Bull. of the Bur. of St. III 305.

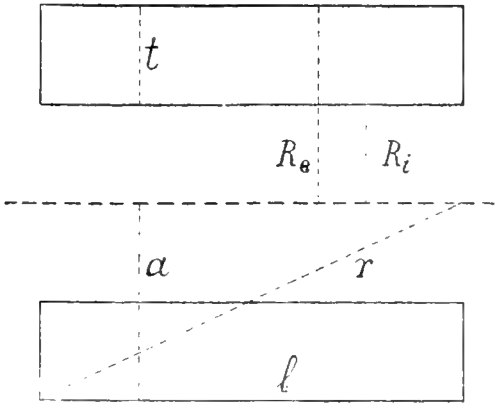

Fig. 1

secutive layers, we get for the radii of the consecutive layers:

$$a_2 = a_1 - \delta a$$
$$a_3 = a_1 - 2\delta a$$
$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$
$$a_m = a_1 - (m-1)\,\delta a$$

The mutual inductance between any two cylinders with radii a_p and a_q being $M_{p.q.}$, the self-inductance of the solenoïd is given by the equation:

$$L_a = 2 \sum_{p=1}^{p=q} \sum_{q=1}^{q=m} M_{p.q} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Substituting the value of a given by (3) in the equation (2) and taking provisionally, in order to facilitate the survey of the derivation, only the two first terms of a with omission of the term $\frac{A^3}{r^3}$, we obtain:

$$M = 4\,\pi^2 n^2 a^2 \left[\sqrt{A^2+l^2} - A + \frac{a^2}{8A}\right]. \quad . \quad . \quad . \quad . \quad (5)$$

In this expression we replace a and A by their above values, a_1, $a_1 - \delta a$ etc. and expand the terms within the square brackets according to ascending powers of δa. We neglect all terms in which δa occurs to a higher degree than the second, and for the above mentioned reason we also omit the terms with $\overline{\delta a}^2$ resulting from the expansion of the form under the radical.

Moreover putting $\sqrt{a_1^2+l^2} = r$ we find for the terms of the integral (4):

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$$\left.\begin{aligned}
M_{1.1} &= 4\pi^2 n^2 a_1^2 \left\{ r - a_1 + \frac{a_1}{8} \right\} \\
M_{1.2} &= 4\pi^2 n^2 a_2^2 \left\{ r - a_1 + \frac{a_1}{8} - \frac{2\delta a}{8} + \frac{\overline{\delta a}^2}{8a_1} \right\} \\
M_{2.2} &= 4\pi^2 n^2 a_2^2 \left\{ r - \frac{a_1 \delta a}{r} - a_1 + \delta a + \frac{a_1}{8} - \frac{\delta a}{8} \right\} \\
M_{1.3} &= 4\pi^2 n^2 a_3^2 \left\{ r - a_1 + \frac{a_1}{8} - \frac{4\delta a}{8} + \frac{4\overline{\delta a}^2}{8a_1} \right\} \\
M_{2.3} &= 4\pi^2 n^2 a_3^2 \left\{ r - \frac{a_1 \delta a}{r} - a_1 + \delta a + \frac{a_1}{8} - \frac{3\delta a}{8} + \frac{\overline{\delta a}^2}{8a_1} \right\} \\
M_{3.3} &= 4\pi^2 n^2 a_3^2 \left\{ r - \frac{2a_1 \delta a}{r} - a_1 + 2\delta a + \frac{a_1}{8} - \frac{2\delta a}{8} \right\} \\
M_{1.4} &= 4\pi^2 n^2 a_4^2 \left\{ r - a_1 + \frac{a_1}{8} - \frac{6\delta a}{8} + \frac{9\overline{\delta a}^2}{8a_1} \right\} \\
M_{2.4} &= 4\pi^2 n^2 a_4^2 \left\{ r - \frac{a_1 \delta a}{r} - a_1 + \delta a + \frac{a_1}{8} - \frac{5\delta a}{8} + \frac{4\overline{\delta a}^2}{8a_1} \right\} \\
M_{3.4} &= 4\pi^2 n^2 a_4^2 \left\{ r - \frac{2a_1 \delta a}{r} - a_1 + 2\delta a + \frac{a_1}{8} - \frac{4\delta a}{8} + \frac{\overline{\delta a}^2}{8a_1} \right\} \\
M_{4.4} &= 4\pi^2 n^2 a_4^2 \left\{ r - \frac{3a_1 \delta a}{r} - a_1 + 3\delta a + \frac{a_1}{8} - \frac{3\delta a}{8} \right\} \\
M_{1.5} &= 4\pi^2 n^2 a_5^2 \left\{ r - a_1 + \frac{a_1}{8} - \frac{8\delta a}{8} + \frac{16\overline{\delta a}^2}{8a_1} \right\} \\
M_{2.5} &= 4\pi^2 n^2 a_5^2 \left\{ r - \frac{a_1 \delta a}{r} - a_1 + \delta a + \frac{a_1}{8} - \frac{7\delta a}{8} + \frac{9\overline{\delta a}^2}{8a_1} \right\} \\
M_{3.5} &= 4\pi^2 n^2 a_5^2 \left\{ r - \frac{2a_1 \delta a}{r} - a_1 + 2\delta a + \frac{a_1}{8} - \frac{6\delta a}{8} + \frac{4\overline{\delta a}^2}{8a_1} \right\} \\
M_{4.5} &= 4\pi^2 n^2 a_5^2 \left\{ r - \frac{3a_1 \delta a}{r} - a_1 + 3\delta a + \frac{a_1}{8} - \frac{5\delta a}{8} + \frac{\overline{\delta a}^2}{8a_1} \right\} \\
M_{5.5} &= 4\pi^2 n^2 a_5^2 \left\{ r - \frac{4a_1 \delta a}{r} - a_1 + 4\delta a + \frac{a_1}{8} - \frac{4\delta a}{8} \right\}
\end{aligned}\right| \quad (6)$$

etc.

The law of succession for the numerical coefficients of the terms *within* the brackets, in each group with the same factor *before* the brackets, is very evident, so that the sum is easily found.

After adding and ranging we find:

$$\begin{aligned}\Sigma\Sigma M_{pq} = 4\pi^2 n^3 \Big\{ & [a_1^2 + 2a_2^2 + 3a_3^2 + 4a_4^2 + 5a_5^2 + \ldots]\left(r - a_1 + \frac{a_1}{8}\right) + \\ & + [\quad a_2^2 + 3a_3^2 + 6a_4^2 + 10a_5^2 + \ldots]\left(\delta a - \frac{a_1 \delta a}{r}\right) + \\ & + [\; 3a_2^2 + 9a_3^2 + 18a_4^2 + 30a_5^2 + \ldots]\left(-\frac{\delta a}{8}\right) + \\ & + [\quad a_2^2 + 5a_3^2 + 14a_4^2 + 30a_5^2 + \ldots]\frac{\delta a^2}{8a_1} \Big\}\end{aligned}$$

The terms 2 and 3 can be combined into one, namely:

$$[a_2^2 + 3a_3^2 + 6a_4^2 + 10a_5^2 + \ldots]\left(\delta a - \frac{3\delta a}{8} - \frac{a_1 \delta a}{r}\right)$$

The infinite series within the square brackets must be integrated. We replace a_2, a_3 ... etc. by their values, $a_1 - \delta a$, $a_1 - 2\delta a$ ... etc. and obtain for instance for the first series:

$$\left.\begin{aligned} a_1^2 &= a_1^2 \\ 2a_2^2 &= 2a_1^2 - 4a_1\delta a + 2\overline{\delta a}^2 \\ 3a_3^2 &= 3a_1^2 - 12a_1\delta a + 12\overline{\delta a}^2 \\ 4a_1^2 &= 4a_1^2 - 24a_1\delta a + 36\overline{\delta a}^2 \\ 5a_5^2 &= 5a_1^2 - 40a_1\delta a + 80\overline{\delta a}^2 \\ & \ldots\ldots\ldots\ldots\ldots\ldots \end{aligned}\right\} \quad \ldots \quad (8)$$

$$ma_m^2 = ma_1^2 - 2m(m-1)a_1\delta a + m(m-1)^2\overline{\delta a}^2$$

The numbers in the vertical ranges, figuring as coefficients of a_1^2, $a_1\delta a$ and $\overline{\delta a}^2$ form arithmetical series of respectively first, second and third order.

The general expression for the sum of m terms of an arithmetical series of the n^{th} order is:

$$S_m = mt_1 + \frac{m(m-1)}{1 \, . \, 2}\Delta_1 + \frac{m(m-1)(m-2)}{1 \, . \, 2 \, . \, 3}\Delta_2 + \frac{m(m-1)(m-2)(m-3)}{1 \, . \, 2 \, . \, 3 \, . \, 4}\Delta_3 + \\ \ldots\ldots + \frac{m(m-1)\ldots(m-n)}{1 \, . \, 2 \ldots n+1}\Delta_n \quad \ldots\ldots\ldots \quad (9)$$

wherein t_1 = first term of the series, Δ_1, $\Delta_2 \ldots \Delta_n$ = first terms of the series of differences, n = the order number of the series.

After adding the terms of (8) we thus obtain an expression of the following form:

$$Pa_1^2 - Qa_1\delta a + R\overline{\delta a}^2$$

wherein P, Q and R are functions of m, which are easily found by substituting in (9) the values of t_1, $\angle_1$, $\angle_2$ etc. obtained from the consecutive numbers in the vertical ranges of (8).

In order to determine the integral (4) the number of layers m has to be supposed $=\infty$; so it is evident, that in the functions P, Q and R, i. e. in the expression (9), we only need to retain the term with the highest exponent.

This term is:

$$\frac{m^{n+1}}{1\,.\,2\ldots n+1}\angle_n .$$

We therefore only have to find the order number of each of the series in the vertical ranges of (8), and the value of the constant difference.

For the term with $\overline{\delta a}^2$ for instance this determination gives:

$$\begin{array}{cccc} 0 &&& \\ & 2 && \\ 2 && 8 & \\ & 10 && 6 \\ 12 && 14 & \\ & 24 && 6 \\ 36 && 20 & \\ & 44 && \\ 80 &&& \end{array} \qquad \begin{array}{l} \angle_n = 6 \quad n = 3 \\ \\ R = \dfrac{6m^4}{1.2.3.4} = \dfrac{m^4}{4} \end{array}$$

In the same way we find: $P = \frac{m^2}{2}$; $Q = \frac{2m^3}{3}$.

The series in the first term of (7) now becomes, if we omit the index of a_1

$$\frac{m^2}{2}a^2 - \frac{2m^3}{3}a\delta a + \frac{m^4}{4}\overline{\delta a}^2$$

Now observing that $m\delta a = R_e - R_i = t$, and reducing the fractions we obtain:

$$\frac{1}{12}\left[6m^2a^2 - 8m^2at + 3m^2t^2\right]$$

or, bringing m^2a^2 outside the brackets,

$$\frac{m^2a^2}{12}\left(6 - 8\frac{t}{a} + 3\frac{t^2}{a^2}\right)$$

Putting $\frac{t}{a} = \varrho$ we finally have:

$$\frac{m^2a^2}{12}\left[6 - 8\varrho + 3\varrho^2\right]. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Operating in the same way with the two other series in (7) we find for the coefficients of the terms with δa and $\overline{\delta a}^2$ successively:

$$\frac{m^2a^2}{12} \cdot \frac{1}{5}\left[10-15\varrho+6\varrho^2\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$\frac{m^2a^2}{12} \cdot \frac{1}{15}\left[15-24\varrho+10\varrho^2\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Substituting the values given by (10), (11) and (12) in the equation (7) and afterwards in (4) we find:

$$L_a = \frac{2}{3}\pi^2 n^2 a^2 m^2 \Big\{ \left[6-8\varrho+3\varrho^2\right]\left(r-a+\frac{a}{8}\right) +$$

$$+\frac{1}{5}\left[10-15\varrho+6\varrho^2\right]\left(t-\frac{3t}{8}-\frac{at}{r}\right)+\frac{1}{15}\left[15-24\varrho+10\varrho^2\right]\frac{t^2}{8a}\Big\} . \quad (13)$$

Now expanding and integrating in the above described manner the other terms of the series a, it appears that each term gives a contribution to each of the terms figuring in the coëfficients of (13).

In consequence of the particular regularity of these expansions it is easy to determine the laws for the succeeding numerical coëfficients of the different series.

In the first term of (13) there appears the series:

$$S_1 : \qquad a\left(\frac{1}{8}+\frac{1}{64}+\frac{5}{1024}+\frac{35}{16384}+ \ldots\right.$$

in the second term

$$S_2 : \qquad t\left(3\cdot\frac{1}{8}+5\cdot\frac{1}{64}+7\cdot\frac{5}{1024}+9\cdot\frac{35}{16384}+\ldots\right.$$

and in the third term:

$$S_3 : \qquad \frac{t^2}{a}\left(\frac{1}{8}+6\cdot\frac{1}{64}+15\cdot\frac{5}{1024}+28\cdot\frac{35}{16384}+\ldots\right.$$

From the derivation of the fundamental equation (3), that can be found in the German edition of MAXWELL, edited by WEINSTEIN, it is evident, that the terms of the series S_1 are formed by the products of the equal order terms of four different series.

It is therefore very difficult to find back the law of succession in the above reduced form of these products.

The law of succession is very simple, viz.

$$\frac{u_n}{u_{n-1}} = \frac{(2n-3)(2n-1)}{2n(2n+2)},$$

which gives for the general term of the series:

$$u_n = \left[\frac{(2n-3)!}{n!(n-2)!}\right]^2 \frac{2n-1}{2^{4n-1}(n+1)}.$$

The terms with $\frac{A^3}{r^3} \cdot \frac{A^5}{r^5} \ldots$ etc. also contribute to each of the coëfficients of (13).

These expansions have been executed for all the mentioned terms of (3) except for the terms with $\frac{A^9}{r^9}$ and $\frac{A^{11}}{r^{11}}$, which after all would be incomplete, these two powers of $\frac{A}{r}$ reappearing in two of the succeeding terms.

After insertion of all these terms and after some simple transformations, equation (13) can be brought in the following form:

$$L_t = \frac{2}{3}\pi^2 n^2 m^2 a^3 \Big\{ C_1 [\varphi_1(x) - 0.8488] + C_2 [\varphi_2(x) + 0.0848]\,\varrho + C_3 [\varphi_3(x) + 0.11]\,\varrho^2 \Big\} \quad \ldots\ldots \quad (14)$$

wherein a = outer radius of coil, insulation included

$C_1 = 6 - 8\varrho + 3\varrho^2$ $\qquad \varrho = \frac{t}{a}$ $\qquad x = \frac{a}{r}$ $\qquad r = \sqrt{a^2 + l^2}$

$C_2 = 10 - 15\varrho + 6\varrho^2$

$C_3 = 15 - 24\varrho + 10\varrho^2$

n = number of windings per cm.

m = number of layers

l = length of coil

$$\varphi_1(x) = \frac{1}{x} - \frac{1}{8}x^3 + \frac{1}{16}x^5 - \frac{15}{128}x^7 + \ldots$$

$$\varphi_2(x) = -\frac{1}{5}x + \frac{3}{20}x^3 - \ldots$$

$$\varphi_3(x) = \frac{1}{30}x - \frac{3}{40}x^3 + \ldots$$

The constants appearing in formula (14) have the following meaning:

$$0.8488 = 1 - S_1$$

$$0.0848 = \frac{1}{5}(1 - S_2)$$

$$0.11 = \frac{1}{15}S_3$$

wherein S_1, S_2, and S_3 represent the sums of the above mentioned series. The first of these constants, which has the greatest influence on the accuracy of the computed values, is accurate within a few units of the fifth decimal place.

The accurate determination of these constants is practically equivalent with including in the integration a very great number of the not mentioned terms of (3).

That in formula (14) m represents the *finite* number of layers, whereas for the integration m is supposed to be *infinite*, depends upon the fact, that the self-inductance, for the case the current is uniformly distributed over the cross section of the coil, is proportional to the square of the number of layers.

For moderate values of ϱ, which quantity in most cases is considerably smaller than 1, the mutual proportions of the coëfficients C_1, C_2 and C_3 are very nearly represented by the mutual proportions of the constants 6, 10 and 15 appearing in these coëfficients. As the terms with ϱ and ϱ^2 for long coils are always *very small* in comparison with the first term we may put approximately:

$$C_2 = \frac{5}{3} C_1 \qquad C_3 = \frac{5}{2} C_1 ;$$

substituting these values in (14), we obtain:

$$L_u = \frac{2}{3} \pi^2 n^2 m^2 a^3 C_1 \left\{ [\varphi_1(x) - 0.8488] + \frac{5}{3} [\varphi_2(x) + 0.0848] \varrho + \right.$$

$$\left. + \frac{5}{2} [\varphi_3(x) + 0.11] \varrho^2 \right\} . \; . \quad (15)$$

Putting in this formula $\varrho = 0$ the terms with ϱ and ϱ^2 vanish and $C_1 = 6$.

We then get the formula for the self-inductance of a cylinder or single layer coil:

$$L_s = 4 \pi^2 n^2 a^3 (\varphi_1 (x) - 0.8488) \quad . \; . \; . \; . \; . \quad (16)$$

The method of testing the degree of accuracy obtained in the computation of self-inductances by means of the formulae (14) and (15) is based on the same principle, as used by Rosa in his above mentioned method.

Rosa [1]) begins with the calculation of the self-inductance of a cylindrical current sheet, which has the same mean radius and length, as the solenoïd with depth of winding t. He takes the total number of windings of this cylinder equal to $\frac{l}{t}$, where l is the common length. Afterwards he considers the solenoïd of length l and depth of winding t as to be formed by one single layer of square conductor, so that the cross section of this conductor is $t \times t$ and the total number of windings is also equal to $\frac{l}{t}$.

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1) E. B. Rosa. Bull. of the Bur. of St. IV 369.

Indicating the self-inductance of the latter by L_u and of the former by L_s, Rosa calculates the correction $\Delta_1 L$ in order to obtain L_u from L_s, so that:

$$L_u = L_s - \Delta_1 L.$$

This correction $\Delta_1 L$ consists of n times the difference of the self-inductance of one winding with square section from that of a winding on the cylinder, added to the sum of the differences of the mutual inductances of all the windings. The correction term $\Delta_1 L$ is brought in the following form:

$$\Delta_1 L = 4\pi a n (A + B)$$

wherein n in the said number of windings $\frac{l}{t}$, $a =$ the mean radius. A is the part of the correction due to the difference in the self-inductance, and B the part due to the differences in the mutual inductances.

Rosa gives two tables, wherein A is given as a function of $\frac{t}{a}$ and B as a function of n.

The error in Rosa's method is concealed in this correction term B, which, as I shall show in a subsequent communication, is not only a function of n but also sensibly depends on the value of $\frac{t}{a}$, so that for this term a table with double entrance would be necessary.

I have computed for a few different values of $\frac{t}{a}$ a table for the term B, by means of which I am able — for these special values of $\frac{t}{a}$ to get an idea about the degree of accuracy that can be obtained in calculating self-inductances by the formulae (14) and (15)

Example 1.

$l = 50$ cM. $a = 5.2$ cM. $t = 0.4$ cM. $m = 4$ $n = 10$

calculated:

by formula (14)	$L_u = 70.5976$	millihenry
,, ,, (15)	$L_u = 70.5988$	,,
,, by accurate correction method	$L_u = 70.5992$	,,
,, by Rosa's method	$L_u = 70.544$	,,
,, by formula (1) of Cohen	$L_u = 70.551$	,,

For this example the correction term used by Rosa is: $B = 0.3440$ whereas the above mentioned table gives: $B = 0.3247$.

The formula of COHEN, as well as ROSA's method give too small values for the self-inductance.

An example of the extreme accuracy, obtained with the very simple formula (16) in computing the self-inductance of a cylindrical current sheet, as compared with the value calculated by the exact formula of LORENZ[1]) with elliptic integrals, may be given here:

Example 2.

$$l = 50 \text{ cm.} \qquad a = 5 \text{ cm.} \qquad n = 10$$

calculated:

by formula (16) $L_s = 4.540489$ millihenry.

„ LORENZ's formula $L_s = 4.540486$ „

Physiology. — *"On the permeability of red bloodcorpuscles in physiological conditions, more especially to Alkali and Earth-alkalimetals".* By Prof. H. J. HAMBURGER and Dr. F. BUBANOVIĆ.

Mr. G. GRYNS has published a short article in this paper[2]), in which on the ground of some calculations he thinks it desirable to object to some of the conclusions we drew from our experiments on the subject mentioned above. (Proceedings of June 25th, 1910).

We feel convinced that his remarks would not have been published, if he had waited for our more explicit communications on this subject, in the "Archives Internationales de Physiologie". As appears from a note on the first page of our paper we had promised these, and they indeed appeared shortly after[3]).

In this treatise a detailed account is given of the experimental method and moreover by way of example a lengthy report is added in an appendix, containing full particulars of *one* of the series of experiments. In these proceedings it is hardly possible to enter into details, especially when, as in this case, extensive investigations are concerned. A detailed description is better in its place in a physiological periodical.

This remark might suffice, but it is perhaps of some use that those who cannot immediately consult the "Archives Internationales" are made acquainted with the mistake of Dr. GRYNS.

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[1]) Bull. of the Bur. of St. V, 41.

[2]) These Proceedings of October 29, 1910.

[3]) La perméabilité physiologique des globules rouges, spécialement vis-à-vis des cations. Archives Internationales de Physiologie. Vol. X. p. 1. Appeared September 24th 1910.

An example taken at random may serve to illustrate this mistake.

We wish to determine the effect of an addition of some water, for instance, on the interchange of the component parts of blood-corpuscles and serum.

For this purpose we took a certain volume of blood. Let us for the reader's convenience assume that this volume amounted te 100 c.c Let us suppose these to contain 40 c.c. of red blood-corpuscles, and 60 c.c. of serum From these 60 c.c. of serum we take 20 c.c., and dilute them with $7^1/_2$ c.c. of water, but now we do *not* add these $27^1/_2$ c.c. of fluid to the rest of the blood, but only 20 c.c., so that the volume of the blood becomes 100 c.c. again. Now it is obvious that it cannot be expected, as Mr. GRYNS does, that the blood treated, will contain the same absolute amount of substances as the original blood, since serum has been kept back. *This* GRYNS *overlooked,* and a similar mistake he made in the calculation of the experiments, in which the serum was made hyperisotonic by the addition op NaCl.

If Mr. GRYNS, avoiding the mistake made by him, repeats the calculation, he will no longer arrive at the conclusion that "the mistakes in our analyses are much greater than the differences upon which our conclusions are based", nor will these calculations afford him grounds for opposing our views as to the permeability of blood-corpuscles.

Physiology. — "*A tumour in the pulvinar thalami optici. A contribution to the knowledge of the vision of forms.*" By Prof. C. WINKLER.

(Communicated in the meeting of 28 January 1911).

The case, which supplied the material for this paper was the following:

F. t. B, aged 22, who entered the hospital on February 25th 1909, was born from healthy parents and did not suffer from any illness before, neither traumata, nor venereal infection. He partook of alcohol and tobacco in a moderate way.

Since Dec. 1908 there was a stiffness of the right leg, followed afterwards by unsteadiness in the movements of the right hand. The commissure of the lips on the right side began to drop. By and by the patient became aware of a peculiar sensation in the right half of the body, a certain numbness, and he commenced to stammer. All these symptoms gradually grew worse without any aching of head or limbs, without dizziness, without disturbances of vision or hearing, as far as the patient knows. Only his memory was impaired.

During March and April notes have been taken about the case. The patient, a very intelligent individual, takes an interest in his surroundings and has right notions as to space and time; the pulse is feeble, 92 per minute, and regular.

Respirations 22 per minute. Nothing abnormal in the organs of the thoracal and ventral region. In the urine neither albumen nor glucose.

Speech is slow, monotonous, stammering and scanned. No disturbances from aphasia or faults of articulation. The patient is able to read and to understand what he reads. Writing is bad (ataxy of the right hand). The pressure on the paper is irregular. The pencil cannot be maintained in the right direction. Still the writing is not illegible, each letter and each word being taken separately. No vestige of agraphy. The head, measuring 53 c.M. in circumference, nowhere aches under pressure.

The sense of smelling is intact. That of hearing is disturbed slightly on both sides, to the right a whisper is heard at 1 M. distance, to the left at 2 M. The sense of taste is impaired.

The pupils of the eyes, unequal, a little more dilated to the right than to the left, are reacting well on light and in converging. The movements of the eyes, except for nystagmus, expecially when looking to the right, can be performed completely. The convergency is not disturbed. The commissure of the lips to the right is drooping, the orbital fissure on that side is wider than to the left. On the right half of the face hardly any folds are to be seen. By active movements, the muscles around the right angle of the mouth are hardly moved at all. The facial muscles react normally on electric stimuli.

The tongue is put out tremulously, pointing to the right. The patient holds his head inclined to the right. The right shoulder droops. The right arm is oedematous, without rigidity or hypotony. All active movements can be made, but they are performed unsteadily. It is impossible to the patient to make both indexes meet. Unsteadiest of all are the movements of the fingers. Fastening or unfastening buttons, taking matches from a box etc., — all this is done in a very clumsy way.

The reflex actions in the right arm are exaggerated. When walking, the right leg is training. To hop on it is impossible. There is neither rigidity nor hypotony. Paresis and ataxia are more marked in the nether portion of leg and foot than in their upper region. With his right foot the patient is not able to put on a slipper, nor to perform the heel-knee test.

To the right the skin-reflexes of abdomen and cremaster are suspended. The reflexes of the knee and the tendon of Achilles are exaggerated, without cloni. A stimulus of the foot-sole to the right is answered by flexion of the small toes and extension of the large one.

Sensibility is disturbed over the whole of the right half of the body.

The sense of touch is only slightly disturbed. Coarse touches are perceived everywhere, subtler ones remain sometimes unperceived.

The sense of pain has suffered much more important alteration. To the right a pin-point is not perceived to be sharp. This hypalgesia passes the diameter of the body for nearly 1 c.M. The subjective statement of the patient is, that the sensations of touches and of painful stimuli are entirely different on the right and on the left. Cold and heat are perceived less clearly on the right than on the left.

What is most disturbed to the right is the deep-seated feeling, and distally still more than proximally. Passive movements of the fingers and toes are not perceived at all. The tactile circles of Weber are much larger on the right than on the left. The patient localizes badly on the right half of the body.

To the right he is astereognostic, e. g. a key given in the right hand is called after long hesitation "a small hammer", a matchbox is called a cork, a ring a six-penny piece. To the left all these objects are recognized immediately.

The patient himself states that he is able to see well. Yet, if a key is held up before him, the left eye being closed, whilst the right eye is kept fixed on a definite point, the object is immediately recognized for what it is, in the left half of the field of vision, but not in the right half. In the same way, if the right eye is closed, a key is not recognized in the right half of the field of vision to the left.

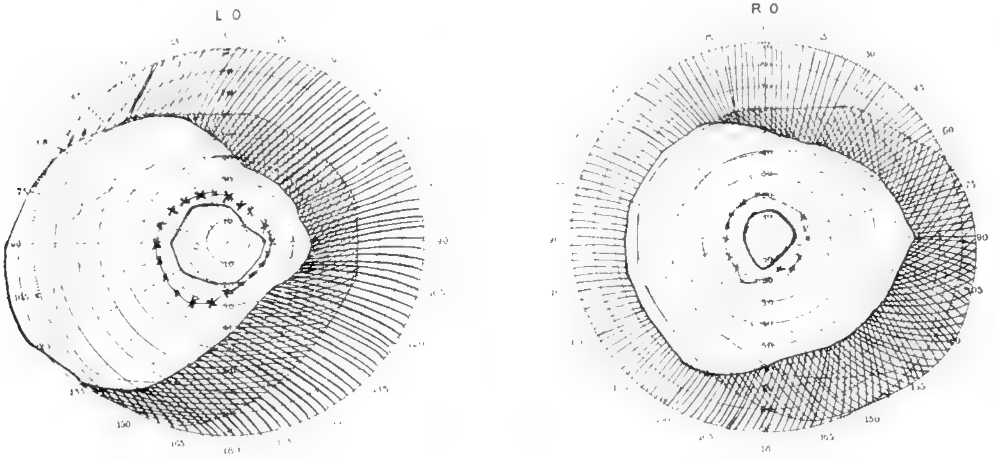
As there is therefore a presumption of hemiopia the patient is examined by the ophthalmologist (Dr. Schmidt), who gives the following statement:

Visus O. D. $^6/_6$, Visus O. S. $^6/_6$, for both eyes $^6/_6$.

A slight restriction of the field of vision for both eyes, but no hemiopia, not for moving objects and not for colours. The fundus presents no aberrations.

This difference led to a more thorough examination, and to the making of different schemes of the fields of vision. The one reproduced here, was taken on April 20th 1909 by Dr. Schmidt, the exterior circle indicating the field of vision for movement, the one marked with crossed lines that for blue, and the inner circle that for red.

Date 20, 4. 1910.



Field of vision for movement, for blue and red on 20. 4. 1910.

At the same time however several figures, measuring 2 c.M. in diameter, were cut out from white cartoon, hearts, circles, diamonds, triangles etc.

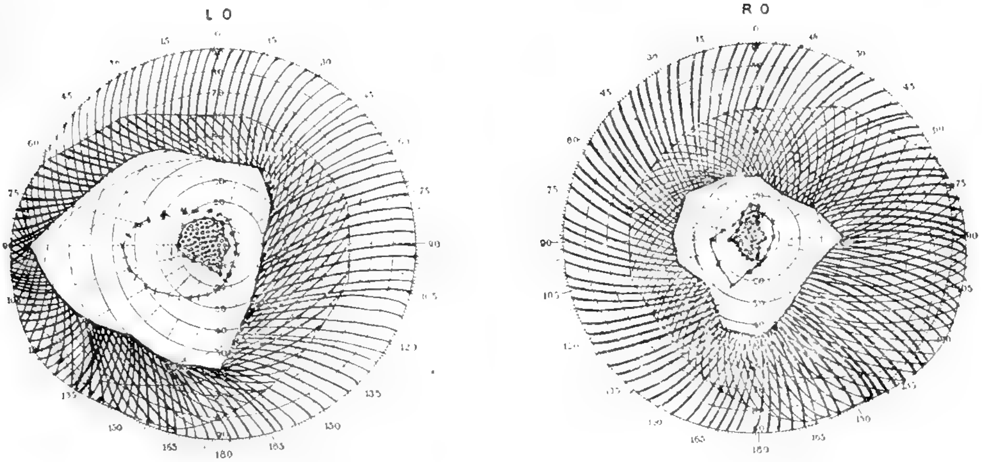
Whenever these different figures were introduced from the left, into the left halves of the fields of vision, they were regularly rightly recognized by the patient at 30°—15° from the fixed point.

But if they were presented to vision from the right, in the right halves of the fields of vision, they never, although the patient saw them approaching, were rightly recognized by him, before they reached the fixed point, or before they had passed the vertical diameter.

The scheme made from this latter experiment, on April 20th 1909, is likewise reproduced here.

The exterior boundary indicates the field of vision for movements, the intercrossed lines mark that for blue. *The area filled with circles is the field of vision, within which the shapes of 2 c.M. diameter are perceived. It follows*

Date 20, 4, 1910.



Field of vision for movement, for blue and for shapes of 2 c.M. diameter.
The field, within which shapes are recognized, is filled with circles.

from this scheme that only in the left halves of the fields of vision the shapes are recognized, not in the right halves.

Gradually the state of the patient grew worse.

Especially the ataxia of the right hand suffered aggravation. With voluntary movements most violent accessory movements were shown. When in rest, the hand assumed a peculiar position. The disturbance in the deep-seated feeling aggravated quickly. The patient was no longer able to localize rightly, his knowledge about the position of the hand was lost and the astereognosy became complete.

Speech too became more difficult.

Still, neuritis optica was not to be stated, and the visual symptoms remained stationary, until on May 15th death occurred suddenly.

At the autopsy, in the left half of the brain was found a tumour, which was yielded in toto to me, thanks to the kindness of Prof. de Vries; on examination it proved to be a glioma. There was made a series of frontal sections of the brain. These sections, treated partly with the Weigert-Pal method, partly with carmine, gave the following data as to the extension of the tumour.

Section 1. It strikes the left hemisphere through the proximal region of the basal ganglia. At the same time it touches the proximal portion of the tumour, which, being but vaguely defined here, perforates the capsula interna, infiltrating the lenticular nucleus and the commissura anterior.

Section 2. It strikes the left hemisphere through the middle of the thalamus, which is enlarged by the tumour, and the right hemisphere through the distal end of the thalamus. The medial and ventral nuclei of the thalamus are substituted by the tumour. The regio subthalamica, together with the red nucleus and fasciculus retroflexus has been pushed ventralward. The field of Wernicke and the retrolenticular capsula interna are not touched by the tumor and have been pushed frontalward and downward.

Section 3. It strikes to the right the distal ending of the pulvinar. The left thalamus is enlarged by the tumour in all directions. The tumour has here taken the place of the pulvinar thalami, destroying at the same time its ventral nuclei with the radiations of the lemniscus entering these nuclei at their ventral surface, and the c. geniculatum internum.

The c. gen. laterale is found to be removed sideward, but otherwise intact. The cells are arranged in it in the ordinary manner, and the intact radiations of the triangular field of WERNICKE (section 2) originate in this intact ganglion (as may be seen in sections between 2 and 3).

In the retro-lenticular capsula interna however an extensive degeneration of fibres towards the parietal gyri is found.

The corp. quadr. anticum has been pushed aside, without being destroyed by the tumour. The tumour pushes aside the radiation from the tractus to this ganglion, but, as is made evident by sections between 3 and 4 the c. quadr. anticum is not infiltrated, although a few fibres in its superficial medullar-layer have degenerated.

Section 4. It strikes the left hemisphere a little before the splenium corporis callosi. The enormous pulvinar, entirely substituted by the tumour, has pushed aside the splenium and the lateral ventricle without injuring their tissues. The tumour has grown together with the posterior portion of the Cornu Ammonis, and is lying therefore, covered by the alveus, within the wall of the ventricle.

Section 5. It strikes the distal end of the tumor. Grown together with the Cornu Ammonis the tumour compresses the ventricle, without injuring its wall.

Section 6. It strikes the occipital lobe circa 1 c.M. distalward from the tumour.

After comparing these different sections, we are justified in assuming *that a tumour, originating in the left pulvinar thalami, growing is distalward, has compressed the posterior horn of the lateral ventricle, is destroying frontalward the ventral and medial nuclei of the thalamus, and is threatening finally the capsula interna, situated more frontally.*

The corpus geniculatum laterale and the fibres passing through the triangular area of WERNICKE, *however are almost completely intact, as is likewise the corp. quadrigeminum anticum.*

In the retro-lenticular region of the capsula interna there are degenerate fibres, part of which pass thence into the strata sagittalia, whilst another part goes directly in the corona radiata of the lower parietal brain, towards the gyrus supra-marginalis (fig. 3, 4, 5).

In the stratum sagittale internum a mass of degenerate fibres is lying laterally from the ventricle and passing gradually through the stratum sagittale externum they enter into the medullary cones of the gyrus angularis and of the basal occipital convolutions.

Remarkable is the aspect of the medullary cones (see section 6) of the circonvolutions around the fissura calcarina. They appear as solid black fascicles.

Nevertheless in both, as well in that of the gyrus cuneus as in that of the gyrus lingualis, there is a stria of degeneration.

In the medullary cone of the g. cuneus this stria is lying dorsally, in the direction of the dorsal portion of the cuneus. The part of the cone situated beneath the cortex in the f. calcarina, is wholly free from degeneration.

In the medullary cone of the g. lingualis the degenerate stria is situated ventrally, directed towards its ventral portion and connected with the degenerate layer of the medullary cones of the occipital gyri. In the g. lingualis too, there is no degeneration in that part of the medullary conus, confining the cortex in the f. calcarina.

Both lips of this fissura, are in WEIGERT-PAL preparations surrounded by black coloured medullary cones.

The tumour found in the left thalamus may aid us to understand the general view of the symptoms of disease.

The present state of our knowledge enables us to conclude that the hypalgesy of the right half of the body, the loss of the deep-seated feeling and the false localisation on that side, the accessory movements and the ataxia of the right hand, and likewise *the astereognosy in the right hand* are dependent on the destruction of the ventral and medial nuclei of the thalamus.

The growing weakness of the right half of the body, the monotonous, stammering speech present indications of the tumour developing frontalward, and perforating the capsula interna.

The destruction of the left corpus geniculatum internum may perhaps be held responsible for the disturbance of hearing on both sides.

Most remarkable however is the disturbance of vision in the patient, as the fundus does not present any abnormal condition. A superficial examination led to a presumption of hemiopia, but after a more careful investigation it became evident that, apart from a slight restriction to the right of both fields of vision, the patient was able to perceive movement and colour in both halves of the field of vision. *On the contrary, shapes are not perceived at all in the right halves of the field of vision.* They are recognised however in the point of fixation and in the left halves of the fields of vision until far towards the periphery.

It ensues that these disturbances are dependent on *a tumour, originating in the left pulvinar, which has destroyed this ganglion together with its medial and ventral nuclei, whilst the corpus geniculatum laterale,* WERNICKE'S *field and the corpus quadrigeminum anticum were left intact by it.*

The shape of an object is recognized best by a normal persons, near and in the point of fixation. Small shapes, comprising many details, the letters and words we read, are even exclusively perceived there and consequently seen with the fovea centralis. Everybody however may ascertain for himself that shapes, measuring 2 c.m. in diameter, will be recognized temporalward unto 40° in the periphery, if they are presented at a distance, equal to the distance of our point of distinct vision.

When the light is bad, the recognizing of shapes in the periphery decreases very quickly in normal persons. Such is likewise the case, when through disease of the N. opticus, there is an important restriction of the field of vision.

Our patient, presenting no abnormal fundus, no disturbance in the perception of light, no blindness for letters or words (no alexia), no optical aphasy, and no other impediment for localizing with the eyes, than nystagmus when the eyes are fixed to the right, does not recognize shapes to the right, however large these shapes may be. This disturbance which incommodes him only very little, is first brought to his knowledge by the doctor. Then he ascertains its existence from the beginning of his disease.

In order to understand this disturbance, it will be necessary to take notice of the studies on alexia, made by NIESSL VON MAYENDORFF [1]).

As the point of departure for his researches this investigator took two facts.

1. Letters and words are recognized only in the neighbourhood of the fovea centralis.

2. Whenever bilateral occipital foci (tumour, softening) determine bilateral hemiopia, there remains a central field of vision, by means of which the patient is able to recognise small forms and colours and to read. On the basis of anatomical arguments, he then proceeds to construct these two propositions:

1. the fovea centralis, projected on the cortex by a special bundle of fibres in the dorso-lateral strata sagittalia a, is localized in a separate cortical area.

2. The destruction of these fovea-fibres or of this cortical area will determine alexia (blindness for letters and writing) either subcortical or cortical.

The first part of this argumentation is not new, but the second part to a certain extent is.

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[1]) ERWIN NIESSL VON MAYENDORFF, Das Rindencentrum der optischen Wortbilder Arch. für Psychiatrie. Bd. 43 S. 633. 1908 and other communications e. g. Ueber eine directe Leitung etc. Wien Kl. Wochenschrift Nov. 1906.

All independent investigators agree on this point, that the fovea centralis must be represented in a special manner on the cortex. They are forced to acknowledge this by the fact, that the hemianopsy determined by occipital foci is always incomplete, i. e. there is still a remnant of the field of vision that has not become blind, and to this remnant belongs the fovea.

Therefore this latter must be represented in a particular way in the cortex.

But there is a great divergence of opinions about the manner in which this particular representation is effected.

Some investigators claim for the fovea a separate cortical area (situated e g. at the bottom of the fissura calcarina, HENSCHEN, SACHS, WILBRANDT).

Others believe the fovea centralis to be localized in a diffuse manner in a very extensive cortical area (to which should belong not only the environs of the fissura calcarina, but also at least the occipital gyri, VON MONAKOW).

This divergence of opinions may easily be understood. After it has been proved (FORSTER, among others) that the patient with bilateral hemianopsia still possesses a central remnant of the field of vision, there remain only two possibilities.

Either in these cases, there remains intact on both sides a cortical area of the fovea, — or the diffuse dispersing of the fibres conducting the fovea-impulses towards an extensive optical cortical field, allows the possibility that even after a relative extensive destruction of cortex and fibres, a certain number of these fibres may have been left intact, and consequently central vision unimpaired.

As however, until now, there were known no well ascertained cases of central hemianoptic scotoma, dependent on accurately demonstrated occipital foci, the partisans of a diffuse localization of the fibres of the fovea have a decided advantage over those, who defend the especial cortex-area of the fovea.

The second, new proposition of NIESSL, interferes in a peculiar way in this dispute.

The field of the fovea of NIESSL is no longer the fovea-field in the fiss. calcarina, as it has been conceived by HENSCHEN among others. The fovea-fascicle of NIESSL irradiates into the dorso-lateral mass of the strata sagittalia, towards the basal occipital gyri and even in the cuneus, not into the calcarina-field but around it.

This fascicle being interrupted (e.g. by a softering focus in the g. angularis or by the destruction of its cortical field), the ensuing symptom will be, no longer a central hemianoptic scotoma, but,

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if the interruption takes place to the left, the non-recognizing of those forms perceived with both fovea, which are connected with the left fascicle.

As the left hemisphere serves especially to the recognition of words that are heard and to speech, subcortical or cortical loss of recognition of the forms used for speech will be the consequence, or in other terms, subcortical or cortical alexia will originate.

In NIESSL's conception the calcarina-region has become a pure optic zone, the light-perceiving zone of the cortex. Here he agrees with CAMPBELL, BRODMANN and others. The surrounding convolutions form the fovea-area. They serve in connection with the optic zone to recognize shapes.

In my opinion this really most ingenious conception of NIESSL VON MAYENDORFF is not affected at all by the dispute, whether or not there exists a special fovea-fascicle situated within the strata sagittalia. But the case described in the foregoing concerns the greater question put forward by NIESSL, if there exists a loss of vision of forms, without a sufficient loss of light-perception.

Shapes are recognized not only with the eye, but also with the hand. More than once there have been stated cases of so called astereognosis, the impossibility to recognize shapes with the hand, though the tactile perception has suffered relatively only a slight disturbance.

Foci within the inferior parietal lobe, (WERNICKE), in the ventral thalamus-nucleus or in its radiation towards this parietal lobe, determine the loss of recognition of forms, without the loss of tactile perception.

In the described case too there was astereognosis of the right hand, corresponding to the destruction of the ventro-medial thalamus-nuclei and to the degeneration of their radiation towards the parietal gyri of the left brain.

It lies near to seek for an analogy between the astereognosis and the above described disturbance in recognizing optical shapes.

If in the ventral nuclei of the thalamus, impulses from the general sensibility (the deep-seated parts of the body) and from the tactile region meet, if there a new entity is composed of those different impulses, which after further activity of the cortex, enters into consciousness as a tactile shape-image, we may assume a similar proceeding to take place for the optical impulses.

For into the pulvinar radiates a fascicle from the tractus opticus. Optical impulses are brought into immediate connection with the kinaesthetic impulses, which are elaborated in the ventral nuclei. The cortical radiation from the posterior regions of the thalamus however lies more backward, it is directed towards the gyrus angularis, the basal occipital convolutions and the cuneus. In this radiation an important degree of degeneration could be demonstrated, but the degenerated fibres do not penetrate into the borders the convolutions, surrounding the fissura calcarina. They are found in the field of the fovea, indicated by NIESSL.

Consequently, although still sufficient optical impulses join the cortex along the corpus geniculatum laterale and the cortical radiation originating from it, yet the cortex, receiving no communication as to the result of the elaboration of several other impulses that should have been prepared in the thalamus, no longer recognizes shapes in the crossed fields of vision.

This analogy holds good only, in as far as the optical sense together with the sense of touch and the kinaesthesia renders the conception of shapes possible.

The eye may also, independently of the sense of touch, recognize shapes, perceive a third dimension etc.

Some time ago, the studies about disturbances in the perception of a third-dimension (Tiefen-Wahrnehmung), which are only sparsely scattered in literature, have been augmented with one by Dr. VAN VALKENBURG. Bilateral foci in the gyrus angularis had determined this disturbance, together with other symptoms, among which alexia.

Although the perception of a third dimension has some relation with the recognizing of shapes in two dimensions, yet it is distinguished from it, as it is likewise from stereoscopic vision.

After the demonstration of VAN VALKENBURG I think it needless to argue this point,

Necessary it is however to recall to mind an interchange of thought, that occurred about this subject between Dr. NIESSL and Dr. VAN VALKENBURG [1]) viz. whether the dorso-lateral region of the strata sagittalia may contain a special fascicle of fovea-fibre. I have stated already that in my opinion, this is not the principal question. The chief point appears to me the question, whether there may be made a division between a light-perceiving field around the f. calcarina and another field enclosing the former, within which, occasionally with the aid of the first field, shapes are recognized.

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[1]) C. T. VAN VALKENBURG. Zur Kenntnis der gestöhrten Tiefen-Wahrnehmung. Deutsche Ztschr. für Nervenh. Bd. 34. S. 322.

NIESSL VON MAYENDORFF. Einige Bemerkungen zu dem Aufsatze des Herrn Valkenburg. Ibidem Bd. 35. S. 165.

VAN VALKENBURG. Kurze Erwiderung auf die Bemerkungen etc. Ibidem Bd. 35. S. 472.

If I am right in my conception, that the degenerated fibres in this case (the borders of the calcarina are intact) are dependent on the destruction of the thalamus and not on the pressure of the enormous tumour on the dorso-lateral portion of the strata sagittalia, there are at any rate strong grounds in favour of it. For the patient showed no symptoms of alexia and there is a continous connection between the tumour in the thalamus and the degenerations having their origin there.

But if this conception be true, this case would apparently aid to support the opinion that in NIESSL's fovea-zone, there entered likewise fibres from the periphery of the retina. For in the case, as described above, the shapes were recognized in the fovea.

If the conditions presented in this case, allow the conclusions that whilst *the perception of light was retained*, shapes could not be recognized hemianoptically, then it must be conceded likewise that NIESSL's fovea-zone contributes also to the vision of shapes with the periphery of the retina.

And this being so, it must be conceded further, that the light-impulses in themselves are insufficient for the recognizing of shapes, that it is only in their connection with other impulses, *a connection prepared within the thalamus*, that they become able to communicate to definite portions of the cortex the data, enabling this latter to recognize shapes.

LEGENDA OF FIGURES.

a.l. = ansa lenticularis. *AM* = cornu Ammonis. *aq* = Aquaeductus Sylvii. *ANG* = gyrus angularis. *br.c.* = bracchium conjunctivum cerebelli. *c.* = sulcus centralis. *c.a.* = commissura anterior. *C.A.* = gyrus centralis anterior. *c.a.f.* = columna ascendens fornicis. *calc.* = fissura calcarina. *c.c.* = corpus callosum. *c.ext.* = capsula externa. *c.extr.* = capsula extrema. *c.g.e.* of *c.g.l.* = corpus geniculatum externum sive laterale. *c.i.* = capsula interna. *cl.* = claustrum. *c.m.* = sulcus calloso-marginalis. *C.M.* = gyrus calloso-marginalis. *C.P.* = gyrus centralis posterior. *c.q.a.* = corpus quadrigeminum anticum. *C.R.* = corona radiata. *C.U.N.* = gyrus cuneus. *f.* = fornix. f_1 = sulcus frontalis primus. *F*I = gyrus frontalis superior. f_2 = sulcus frontalis secundus. *F*II = gyrus frontalis secundus. *F*III = gyrus frontalis inferior. *f.o.* = fasciculus fronto-occipitalis. *f.r.* = fasciculus retroflexus. *FUS* = gyrus fusiformis. *h* = sulcus Hippocampi. *H* = gyrus Hippocampi. *hab.* = habenula. *INS.* = insula *Reylii*. *i.p.* = sulcus interparietalis. *l* = lemniscus *L*I = globus pallidus nuclei lentiformis. L_2, L_3 = putamen nuclei lentiformis. *LI* = gyrus Lingualis. *n.c.* = nucleus caudatus. *n. ant* = nucleus anterior thalami. *n.l.* = nucleus lentiformis. *n. lat.* = nucleus lateralis thalami. *n. med.* = nucleus medialis thalami. *n.ventr.* = nucleus ventralis thalami. *n.ret.* = nucleus reticularis (Gitterschicht) thalami. *n.r.* = nucleus ruber. o_1 = sulcus occipitalis primus. O_1 = gyrus occipitalis primus. o_2 = sulcus occipitalis secundus. *O*II = gyrus occipitalis secundus. o_3 = sulcus occipitalis tertius. *O*III = gyrus occipitalis tertius. *o.p.* = sulcus occipito-parietalis. *ot* — sulcus occipito-temporalis. *OT* = gyrus occipito-temporalis. *P*I = gyrus parietalis superior. *PAR* = gyrus paracentralis. *p.c.* = sulcus post-centralis. *p.P.* = pes pedunculi *p.o.* = sulcus parieto-occipitalis. *p.r.* = sulcus praecentralis. *PRC.* = gyrus praecuneus. *p.s.* = sulcus parietalis superior. *S* = fissura Sylvii. *S.M.* = gyrus supramarginalis. *s.n.* = substantia nigra. *s.olf.l.* = stria olfactoria lateralis. *s.s.i.* = stratum sagittale internum. *s.s.e.* = stratum sagittale externum. t_1 = sulcus temporalis superior. *T*I = gyrus temporalis superior. t_2 = sulcus temporalis secundus. *T*II = gyrus temporalis secundus. t_3 = sulcus temporalis tertius. *T*III = gyrus temporalis tertius. *tap.* = tapetum. *tr.o.* = tractus opticus *V* = ventriculis lateralis. *v. d'Az.* = fasciculus *Vicq-d'Azyr*. *W* = Wernicke's field.

Physics. — *"The Rectilinear Diameter for Oxygen"*. By E. Mathias and H. Kamerlingh Onnes. Communication No. 117 from the Physical Laboratory of Leiden.

(Communicated in the meeting of June 25, 1910 and January 28, 1911)[1].

§ 1. *Introduction.* As far back as Dec. 1894 the comparison of the equation of state for the permanent gases (particularly that for hydrogen) with the equation for ordinary normal substances was mentioned in Comm. N°. 14 dealing with the Leiden cryogenic Laboratory as being one of the first objects for which efforts were made to develop the methods now used for obtaining accurate measurements at very low temperatures. While the law of corresponding states was assumed to be approximately correct for the group of substances of very low critical temperature as well as for the other normal substances, there were still reasons for suspecting that their reduced equations of state would show deviations on comparison with those of other substances greater than are found between various groups of ordinary normal substances. In fact, the reduced empirical equation of state for ordinary bodies differs considerably from the original reduced equation of van der Waals; nor does this difference disappear when the equation is modified by making a calculation of the influence on the kinetic pressure of the finite dimensions of the molecules stricter than that developed by ascribing a constant value to *b*. At that time the hope could be cherished that substances such as oxygen, nitrogen, and hydrogen would, on account of the simpler constitution of their molecules, show a better correspondence with the assumptions upon which van der Waals based his calculations, and that their reduced equations would approximate to the theoretical van der Waals equation, showing at the same time deviations from the reduced equations for the other substances.

Operations intended to throw light upon this subject made but slow progress[2]). Cryostats had to be constructed that put a range of

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[1]) An excerpt from this paper appeared in the C.R. July and Aug. 1910. The Académie des Sciences at Paris has shown its great interest in the study of the rectilinear diameter of liquids which exist at very low temperatures only, in granting one of us a subvention from the Bonaparte Fund so as to be able to come to Leiden. It is an agreeable duty to record our cordial thanks for this.

[2]) See introduction to Comm. No. 97*a* (March 1907).

sufficiently accurate temperatures at our disposal: the liquefaction of hydrogen soon appeared upon the programme: the piezometry and thermometry of low temperatures had to be studied. In the meantime were discovered the monatomic gases whose molecules probably answer best the assumptions made by VAN DER WAALS, and helium at once usurped the place originally set apart for hydrogen. And now helium itself has been liquefied, but the number of isotherms of different gases that have been determined is small while the region covered by them is narrow, and although the problem that is being worked out at Leiden has undergone important extensions, it still retains the same character as before.

Helium is now the substance to which one would *a priori* ascribe an equation of state most resembling the VAN DER WAALS equation. In this connection it remains to be shown how, from the surfaces which represent the reduced equations of state for ordinary normal substances (passing over first those for oxygen, nitrogen, etc. argon, then those for neon and hydrogen) that for helium may be derived by continual deformation: to this one would like to ascribe a limiting form.

Comms. No. 71 (June 1901) and 74 contain a reduced equation of state obtained by combining the different portions given by various measurements with hydrogen, oxygen, carbon dioxide, ether and isopentane, each for the region of reduced temperature which corresponds with the ordinary temperature for that particular substance. In the Leiden researches this mean equation of state is regarded as an envelope which is in contact with each of the special surfaces of state in that region to which it has contributed to form the mean equation, while the special reduced surfaces for the various substances separate from each other and from the enveloping surface in the other regions, the helium surface in this respect exhibiting the greatest deviations. In fact, the special reduced equation for hydrogen [VII, H_2, Comm. No. 109*a* § 7 equation (16), March 1909] differs markedly from the mean (VII, 1, Suppl. No. 19, p. 18), and measurements already made with helium (cf. Comm. No. 108, Aug. 1908) confirm the fact that its equation of state differs from that for hydrogen in the same way as this has been found to differ from oxygen and nitrogen.

The deformation of the surface representing the reduced equation of state is accompanied by a deformation of all corresponding lines on it, thus occasioning a change in the reduced values of all magnitudes deduced from the equation. This point will be treated in greater detail in an article by H. KAMERLINGH ONNES and W. H. KEESOM on the equation of state and its graphical treatment in the Encyklopädie der Mathematischen Wissenschaften.

One of the most important of these reduced magnitudes seems to be the rectilinear diameter. In 1899[1]) it was shown that the law of corresponding states was not true as regards the diameter for substances as a whole. On the supposition that the diameter is also a straight line for substances of very low critical temperature, the measurements made by DEWAR and by WROBLEWSKI show that for these substances the reduced slope differs greatly from that for ordinary normal substances. This result led to the expectation that the investigation of the diameter would reveal a characteristic feature of the whole representation of the differences between the equations of state for substances of low critical temperature and those for ordinary normal substances, and this the more so as VAN DER WAALS' recent researches upon molecular conglomerations in the liquid state have brought the rectilinear diameter to the front as a means of determining the law governing such conglomerations.

In an investigation of the diameter of substances of low critical temperature the first question encountered is the following. It has been shown that for ordinary normal substances the diameter is straight to a high degree of approximation: is this also the case for substances of low critical temperature? Does the deformation of the reduced surface, while occasioning a change in the orientation of the diameter, leave unaltered its rectilinear nature as ought to be the case if this straightness were intimately connected with the innate characteristics of the liquid state? This is the fundamental problem that we have attacked, and it is answered in the affirmative by the measurements on oxygen which we publish in the present paper[2]).

Oxygen[3]) was very suitable for this first investigation as it remains liquid down to a very low reduced temperature (0.30), and with the cryostat and the thermometric apparatus that had been prepared for the investigation of the isotherms we have mentioned, we were able to trace the diameter from the critical point down to — 217° C. (reduced temp. 0.36).

If one were to leave neon and helium out of the question as affording too many difficulties for an investigation of this kind, then liquid densities at still lower temperatures could be obtained with hydrogen only. As yet, however, a cryostat for hydrogen is wanting

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[1]) E. MATHIAS. Liège Mém. Soc. Roy des Sc. 2 (1899).

[2]) The results were already given in the excerpt published in C.R. July-Aug. 1910.

[3]) Measurements of the density of liquid oxygen were announced Comm. N⁰. 95b (1906) pg. 28 note 1.

for temperatures between its boiling point and its critical point, so that measurements for the most important portion of the diameter viz. that part lying between the boiling point and the critical point, are not yet possible, and only that part of the diameter lying below the boiling point, which we may term the produced diameter, is available for measurement.

A final reason for the use of oxygen is that it can be easily prepared in a perfectly pure condition. This was done by heating potassium permanganate contained in tubes forming part of an apparatus made completely from glass. The oxygen liquefied in another part of the apparatus that was immersed in liquid air, and was then distilled from this apparatus into a cylindrical reservoir (see § 4) that was in its turn cooled in liquid air. The quantity of liquid condensed in this reservoir was so regulated that when the ordinary temperature was reached again, the safe pressure allowed by the construction of this copper cylinder was not exceeded.

§ 2. *First Method. Densimeter.* We deduced the constants for the diameter from measurements of the densities of the liquid and of the vapour at a series of different temperatures. At every density determination for both liquid and vapour the phase whose density was being determined was kept in equilibrium with a small quantity of the coexisting phase.

Fig. 1 Pl. II represents an apparatus with which the diameter can be directly determined. Two equal reservoirs A and B are connected by means of a graduated capillary c; the upper reservoir ends in a narrow capillary coupled to a tap f. The internal volume of the apparatus as far as one of the divisions d is twice the volume of the lower reservoir as far as one of the divisions on the capillary c. The dilatometer is now filled so that at the lowest temperature employed, the liquid meniscus stands at the central mark: the temperature of the apparatus is then raised and each time this is done so much of the vapour is allowed to escape through the tap f that the liquid meniscus always touches the central line. The quantity of oxygen contained in the apparatus at the lowest temperature and the quantities which are successively allowed to escape on proceding to other temperatures are measured, and corrections are applied for the narrow capillary e, for the difference between the nominally equal volumes V_A and V_B of the two portions A and B and also for the difference between the liquid level and the central mark, and then the data for the diameter are at once deduced from the equation $V_A \varrho_{liq} + V_B \varrho_{vap} = V_A (\varrho_{liq} + \varrho_{vap})$, where V_A is known.

We have not yet used this apparatus, but as we have already mentioned we made use of the less direct method of determining ϱ_{liq} and ϱ_{vap} separatedly for the same temperature, sometimes adding determinations of the difference $\varrho_{liq} - \varrho_{vap}$.

To determine ϱ_{liq} and ϱ_{vap} a glass reservoir of known volume is filled with the phase to be investigated, while a small quantity of the coexisting phase is allowed to be present. This reservoir is joined to a narrow glass capillary, which allows it to be immersed in a bath of liquefied gas in one of the cryostats of the cryogenic laboratory. The glass capillary is continued by a narrow steel capillary that can be closed by a tap. Since the measurement of the quantities of gas filling the densimeter is, as will be seen in § 3, made in a volumenometer, it would seem desirable to make use of different reservoirs if the densities of the liquid and vapour are to be determined with the same degree of accuracy; but for the purpose of our measurements this was not necessary. To determine a point on the diameter it is not necessary to obtain such a high percentage accuracy in the density of the vapour as in that of the liquid; it is sufficient if the quantity filling the reservoir used for both determinations is known with the same absolute accuracy in each case. Hence the same reservoir may be used for determining ϱ_{liq} and ϱ_{vap}.

As the determination of the vapour density necessitates an accurate knowledge of the volume of liquid that is left in equilibrium with the vapour, the reservoir of the densimeter terminates at its lower extremity in a graduated appendix a. Unfortunately, the capillary chosen for this appendix was so narrow that in the course of the measurements it was necessary to take the level of the liquid in the conical portion of the capillary above the graduation. In these circumstances it was rather difficult to obtain this correction [1].

The shape of the reservoir was so chosen that the method of constant mass as well as that of constant volume could be employed. With this end in view the reservoir consisted in part of a graduated stem d_e—d_e; thus the apparatus formed a dilatometer provided with a very narrow capillary d_f and a tap k_6, as well as an appendix d_a. While the tap k_6 remains closed, the liquid meniscus that at the

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[1] This was done in the following way: Copies were constructed from pieces of the same kind of glass to exactly the same external dimensions, and of such internal dimensions as to be optically identical. These copies were then subjected to successive grindings and the internal dimensions were taken after each grinding; the volumes were then determined by integration. We gratefully acknowledge our indebtedness to Mr. G. Holst for the care which he devoted to this part of the investigation.

first temperature stood at the highest mark on the stem which we may call η_{l_1} sinks as soon as we proceed to lower temperatures. The levels of the liquid $\eta_{l_2}, \eta_{l_3} \ldots \eta_{l_n}$ corresponding with the constantly decreasing temperatures $T_2, T_3 \ldots T_n$ are read with a cathetometer microscope until at last the level of the liquid sinks beneath the stem d_e—d_e (Pl. II. fig. 2). To turn these measurements to the best advantage, the dimensions of the appendix d_a must be so calculated that when the tap is closed for determinations of the densities of the vapour at the temperatures T_1, T_2, $T_3 \ldots T_n$ readings of the level $\zeta_1, \zeta_2, \zeta_3 \ldots \zeta_n$ in the capillary of the appendix can be made. In that case one can calculate directly the corrections that must be applied to the rough values of $\varrho_{liq_1}, \varrho_{liq_2} \ldots \varrho_{liq\,n}$ and ϱ_{vap_1}, $\varrho_{vap_2} \ldots \varrho_{vap\,n}$ which are obtained by neglecting the correction for the small quantity of the coexisting phase, whereas otherwise these corrections would have to be determined by successive approximations¹). The condition essential to the successful application of the simple method viz. that accurate equality may be realised between the cryostat temperatures at which the liquid and the vapour densities are determined, was fulfilled in our experiments, and so there was every reason to make use of this circumstance in our application of the method of constant mass to temperatures between T_1 and T_n.

As determinations of mass in the case of a permanent gas necessitate rather difficult measurements, it can be seen that the number of separate mass determinations necessary when the constant volume method (that in which the dilatometer from a mark on the appendix to the uppermost mark on the stem functions as a densimeter) is exclusively used, ought to be limited to as narrow a temperature range as possible. For this reason the dilatometric method (of constant mass) is combined with the densimetric (or pyknometric) method of constant volume: the former method as indicated above gives the data necesary for a series of intermediate temperatures, while the latter affords, as it were, the standard points in the range of temperatures to be traversed between which intermediate points are inserted to correspond with temperatures occurring between two standard points.

For oxygen, and this is in general the case with the permanent gases, neither the constant mass method nor the constant volume method can be rigorously applied over the whole range of temperatures. To traverse the various regions of temperature it is sometimes necessary to change from one temperature bath to another and this can only happen by exposing the apparatus

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¹) E. Mathias. Remarques sur le théorème des états correspondants. Ann. de Toulouse 1891.

to the ordinary temperature in between. To do this it is necessary to allow the gas to escape from the dilatometer and then allow it to return when the second low temperature has been established. For measurements with oxygen the lowest temperatures are given by a bath of liquid oxygen, from — 217° C. to — 183° C., temperatures between — 183° C. and — 164° C. are obtained with a bath of liquid methane, and temperatures between — 164° C. and — 120° C. with a bath of liquid ethylene. In this way one must begin with a new quantity of material at least three times. Hence some standard points on the temperature scale are given by the nature of the bath itself.

On the other hand a change of apparatus on proceeding from one region of temperature to another would be a decided advantage from the point of view of obtaining greater accuracy. The expansibility of the liquid and the density of the vapour increase rapidly as the critical temperature is approached: it is clear that if one did not wish to be confined to too small an interval in using the same dilatometer over this region, one would choose varying diameters for the stem and for the appendix. For this reason we constructed a series of dilatometers with different stems and different appendices calculated for a series of temperature intervals. Dilatometers that had to be used at temperatures nearer the critical had appendices and stems of greater diameter than the others. Furthermore, by constructing our dilatometers of two parts united by a graduated capillary we tried to provide ourselves with as many controls as possible, for by this device we should be able to check direct measurements made with each of the individual apparatus with one or more of the measurements that were made with another.

In our first experiments we avoided the complications which we have just described and which are encountered as soon as one attempts to obtain for all the data for the diameter the greatest accuracy possible considering the constancy of the cryostat temperatures and the degree of accuracy with which these can be measured. For this reason we made all our measurements both of vapour density and of liquid density with the same dilatometer, whether they were at very low temperature or in the neighbourhood of the critical. Hence this dilatometer was so constructed that it could withstand the critical pressure. The great advantage in using a single dilatometer for all the determinations lay in the fact that as soon as it was in its place in the cryostat, one had only to pour in the various liquefied gases necessary for the different baths to be able to traverse the whole range of temperature, and that without having to alter the measuring apparatus in any way during the whole series of determinations. It was also of the highest importance that the densities necessary for the calculation of the diameter should be obtained with the same accuracy over their whole course, while, on the one hand, the largest quantity of gas which we could use for each measurement was limited by the dimensions of the volumenometer, and on the other hand, the accuracy of the measurements at the highest temperature was limited by the degree of constancy of the temperature itself. Moreover, there was no necessity for obtaining a greater degree of accuracy for individual points than that which is possible by this method and which may be represented by a unit in the third decimal place. This accuracy is sufficient to determine if the diameter for oxygen is to be considered as straight, and to deduce its slope with the same accuracy as that with which it has been determined for other substances. In any case this first step was desirable in order that data might be obtained to serve for the calculation of the other apparatus mentioned, and to be useful in leading to a greater degree of accuracy. For the degree of accuracy desired it was seen that it was not necessary to determine vapour densities at the lowest temperatures, for it may be assumed that these densities can be calculated with sufficient accuracy.

The dilatometer is seen in position in the cryostat *Cr* in the diagrammatic plan shown in Plate I, its exact dimensions are given on Plate II, fig. 2. The method of joining the glass capillary d_f to the steel capillary d_q of about 0.6 mm. diameter is described in Comm. N°. 69 (April 1901) Pl. II, fig. 4. The piece d_{f4} is soldered to the glass in the manner described in Comm. N°. 27 (June 1896); its end surface is ground perpendicular to the stem; instead of a leather ring steeped in wax a fibre ring was used as packing. This connection as well as all other metal connections and taps are kept under test by immersion in oil — a method introduced in Comm. N°. 94*b*, June 1905; this is done by means of a tube attached at *a* to the cover of the cryostat in which the dilatometer is placed (see Pl. II fig. 2 and Pl. I).

§ 3. *Method II. Volumenometer.* The mass of the gas was determined volumenometrically. We used the accurate volumenometer described in Comm. N°. 84 (March '03). Since then it has undergone some modifications for experiments by KAMERLINGH ONNES and DE HAAS on the compressibility of hydrogen vapour at and beneath its boiling point, the results of which will soon be published. The reservoir for the preparation of mixtures (Comm. N°. 84, Pl. II, fig. 2) which may be seen in use in the apparatus used for the experiments of Comm. N°. 88 (Jan. '04) and N°. 92 (Sept. '04) was needed neither for our present experiments nor for those on the compressibility of hydrogen vapour. The reservoir F' (F of N°. 84, Pl. II) has a separate mercury holder Q_2 (Pl. I) and the capillary connecting this reservoir with the volumenometer is so constructed that the gas contained in it may be driven completely out by the mercury. A second tap k_1 was put in the fork of the tube connecting the volumenometer with the reservoir F'; when gas has been admitted into the volumenometer from the reservoir F' the mercury is allowed to rise above the tap k_2 of the reservoir F' and in the volumenometric determinations the volume of the mercury that has risen in k_1—k_2 is allowed for by reading the position of the mercury from the graduations of the calibrated capillary.

The dead space consists of the portion of the volumenometer that projects above the level (ξ in Pl. I) of the liquid in the bath in which it is placed, and of the spaces between the volumenometer and the taps of the apparatus that are connected with it (for instance, k_4 and k_5 Pl. I) (and usually too, the dilatometer containing that portion of the gas that remained after the greater part had been transferred to the volumenometer), but the great advantage of constructing the reservoir F' in the above way lay in the fact that in the calculation of the masses that are measured, this dead space occurs only at low pressures, so that it is not necessary to determine its temperature so accurately. In fact, nearly all the gas to be measured can be transferred to the reservoir F' which is evacuated beforehand and then filled with mercury, and if the volumenometer is used as if it were a pump there remains to be measured in the dead space only gas that is at a very low pressure. Then, keeping k_3 closed, the volumenometer is evacuated through k_4 and k_{13}, and the gas that has been stored in the reservoir F' is transferred to it; this large quantity is then measured at a temperature that is known with great accuracy.

The connections between the manometer tube M and the large reservoir R in which a pressure is sustained equal to, or if one so desires, slightly different from atmospheric had also undergone some modification for the research on hydrogen vapour compressibilities. Amongst other alterations we may mention that the connections which are to withstand a vacuum are either ground or fused together so that it is possible to measure volumes over the whole volumenometer at all pressures between 0 and somewhat more than one atmosphere. Moreover, a connection may now be made between the upper portion of the manometer tube and the tube of the volumenometer. By this means control measurements are possible when the pressure is the same (and in particular when it is zero) above the mercury in the two portions of the apparatus, which then form two communicating vessels for the mercury; in that case, apart from other corrections, the mercury menisci must stand at the same height. Another control consists of determining the barometric height which is read from *Bar* (Pl. I) by producing a vacuum above the mercury in the volumenometer. These controls allow one to judge the accuracy of the data that are necessary for the calculation of the corrections. The uses to which the clips l_1, l_2, l_3, l_5 and the taps k_1, k_2, k_3, k_4, l_6 and l_9 (during part of the observations the latter two were replaced by clips) were put during the volumetric operations and particularly during the control measurements just mentioned need no further description. We may also mention that two pieces of wood were used to compress the rubber tube by being screwed closer together and thus cause the mercury to rise a little so that (following RAYLEIGH's method) menisci that were easily readable could be obtained in the desired position: the clips themselves could also be used for the same purpose. For further details regarding the volumenometer and its working we may refer to the papers already mentioned and also to the forthcoming Communication announced in § 3.

The volumenometer has twice been calibrated below the zero mark, once for the experiments published in Comms. Nos. 92 and 88, and again for the experiments by KAMERLINGH ONNES and DE HAAS on the compressibility of hydrogen vapour. The difference between these two calibrations was less than $^1/_{20000}$. In this we have allowed for the fact that the temperature of the upper portion of the volumenometer (above the level ξ) differs from that obtaining in the bath surrounding *E*. For the purpose of the compressibility research the volume of this upper part has undergone some modification, and we have ourselves calibrated the volumes x and x' above the zero mark. We have also used the volumenometer itself to calibrate the dead spaces k_1—k_2, k_3—k_4—k_5, and in this, amongst other things, we allowed for the number of times that a tap has been turned on being opened. By the general application of the method we have given of allowing only a low pressure in these spaces a knowledge of their volumes with the accuracy that is attainable by adopting these measures is necessary only in exceptional cases.

The pressure of the gas whose volume is fixed by bringing the mercury meniscus in the volumenometer to one of the marks made for this purpose is given by the difference of level between the mercury in the volumenometer and that in the manometer tube *plus* the barometric height when, as was the case in all our experiments, this manometer tube is in connection with the constant pressure reservoir R. The height of the barometer was given by *Bar.* (For this method see Comm. No. 60, Sept. 1900, and Comm. No. 84). As a rule the tap k_{13} was opened while equilibrium was being obtained between M and E; it was kept closed while readings were being made. Sometimes, when one wanted better adjustment or readings, advantage was taken of the tap k_{13} to make the pressure in R a few centimeters higher or lower than atmospheric.

§ 4. *Experimental method. Auxiliary apparatus.* A tap k_5 connects the volumenometer with a rigidly constructed T-piece which through other taps connects the volumenometer and the dilatometer with each other and with the apparatus in which the oxygen is stored under high pressure; these are a cylindrical reservoir P_1 and an auxiliary compressor A in the glass tube of which marked A_2 the oxygen is contained over mercury. All parts of the apparatus can be evacuated along k_{43}, k_4, k_5 and this is of course always done, and k_{9b} and c_5 kept closed before any measurements are made and before any oxygen is admitted to the tube A_2 from the reservoir P_1. When, as is almost always the case at very low temperatures, the pressure in the reservoir P_1 is higher than the maximum vapour pressure of oxygen at the temperature of the dilatometer, the oxygen can be simply distilled over into the dilatometer from the reservoir P_1, and by regulating the taps, the liquid can be brought to the desired level in the graduated stem of the dilatometer. The auxiliary compressor is brought into use in making the adjustments when the pressure in the reservoir is lower than that of the liquid oxygen in the dilatometer. The auxiliary compressor, indeed, by closing k_5, k_9 and opening k_8, k_7, k_6 may be coupled to the dilatometer d in Cr to form a piezometer such as is used for the determination of isotherms (see Comms. No. 97*a*, Pl. I and No. 69 Pl. I and II): oxygen is then admitted to the reservoir along k_{9b}, k_9, k_8 and is then transferred to the dilatometer d by forcing mercury into the reservoir by means of compressed air (compare the Plate quoted from Comm. No. 97*a* with that given with the present paper; the letters used are the same in the two cases and their meaning will be found in that Communication); the oxygen is then brought to the desired height in the dilatometer by the admission or removal of oxygen. At the same time one can bring the mercury in A to the graduated part of the stem A_1 by allowing oxygen to return to P_1 if necessary. The auxiliary compressor is evacuated before the admission of mercury; it may also be used in conjunction with a metal manometer previously calibrated with the open manometer of Comm. N°. 44 or with the closed manometer of Comm. N°. 78 [1]) and with the pressure gauge and scale C (see Pl. I) for reading off the vapour pressure, of the liquid oxygen in the dilatometer. This measurement is made while the meniscus is in the middle of the dilatometer reservoir d_b, and care is taken to see that equilibrium, as shown by the stationary condition of the meniscus in A_1 is obtained at the same pressure, when there remains but a very small quantity of liquid in the dilatometer; from this it is seen that the temperature is the same over the whole dilatometer, and in particular that it is the same for the appendix and for the middle of the bath where the temperature is measured.

The copper cylindrical reservoir P_1 with the tap k_{9b} is of the type that is commonly used in the cryogenic laboratory; to it is attached a small manometer, the pressure on which shows the quantity of gas that is still left in the reservoir. The oxygen that has been used for the measurements can be brought back again by distillation on immersing the reservoir in liquid air. The space between k_9 and k_{9b} is used for taking definite small quantities of gas from P_1.

For a detailed description of the arrangement of the cryostat Cr (Pl. I of this Communication with the same letters as in Comm. N°. 97*a*) and for particulars regarding the cycle of liquid gas that is used when the bath that is being worked with is liquid oxygen boiling under reduced pressure, we may refer to Plate I of Comm. N°. 97*a* (March 1907) and to Comm. N°. 94*d* (June 1905). For the cases in which the temperatures are given by baths of liquid methane and liquid ethylene the apparatus is the same in principle. The place occupied by the piezometer in the researches to which reference has just been made is now taken by the dilatometer d. Instead of a single resistance thermometer as was used in Comm. N°. 94*d* we now used two platinum resistance thermometers[2]) each of them with four leads and of the type constructed wholly of platinum and glass (see Comm. N°. 99*b* § 2): the glass cylinder was heated until it was beginning to become slightly soft and then the very fine platinum

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[1]) We wish to record our thanks to Dr. C. DORSMAN and Mr. G. HOLST for the care with which they executed this work.

[2]) The resistance thermometers were calibrated and the temperature determinations were made by Mrs. DE HAAS—LORENTZ: we gratefully acknowledge the careful assistance she gave us in this.

wire was wound on it while it was still hot, the ends of the platinum wire were fused into the glass and then each of them was welded in the blowpipe to two platinum leads.

In the present instance the cryostat vessel was a transparent double-walled vacuum glass. In order to keep the lowest temperature always in the bottom of the cryostat by diminishing the evaporation it was surrounded by a second transparent vacuum glass containing liquid air; the latter was protected from precipitation of mist on its outer surface by another glass filled with alcohol whose temperature was kept above the temperature of the room. (Cf. e. g. Comm. N°. 108).

When the equilibrium that was wanted for a measurement has been reached and the temperature measured while the equilibrium has been maintained, the tap k_6 is closed, the volumenometer and the dead space evacuated (keeping k_7 closed) and then the gas is removed from the dilatometer to the volumenometer.

The temperature of the volumenometer is kept constant by a stream of water delivered by the thermostat described in Comm. N°. 70. Thermometers of the requisite accuracy for each measurement were placed at θ_A in the bath and also at $\theta_B \ldots$ where they were bound to the tubes etc. and were as far as possible wrapped along with them in one common layer of wool.

The volumenometer, the manometer tube with scale alongside and the two limbs of the barometer *Bar* are so disposed around a three telescope cathetometer (Comm. N°. 60) that they can all three be read in succession by simply turning the cathetometer round its axis. To facilitate adjustment the barometer and the scale are placed on small tables (Comm. N°. 95*e*) which allow of horizontal motion by screw travels, and which can undergo alteration with respect to the vertical. Electric lamps serve to illuminate small vertically movable screens with slits placed behind the menisci, or, in conjunction with mirrors, to illuminate other points; they are switched on in succession from a dial close to the cathetometer from which place the screens too can be adjusted to the desired height. For particulars as to the precautions adopted during the measurements we refer to the Communications already mentioned.

§ 5. *Calculation of experimental results, corrections.* The dilatometer was calibrated with mercury. For this purpose there was temporarily fused to d_a (Pl. II fig. 2) a small glass tap with a capillary that was immersed in a tray of mercury. The volume of the meniscus was allowed for from the data given in Comm. N°. 67 (Dec. 1900 and Jan. 1901); for most menisci it is sufficient to regard them as segments of a sphere. The expansion of the glass was corrected for from the data of Comm. N°. 95*b*. The positions of the liquid in the dilatometer stem must be corrected for the liquid in the ring-shaped meniscus that rises up against the glass; to determine this correction we first got the height by an estimation with the micrometer eyepiece or by a measurement made with the micrometer wire of that eye piece; it is very difficult, however, to fix the base of the meniscus. In the end we used the results obtained by graphical calculation of the meniscus from the laws of capillarity [1]).

Finally, to determine the quantity of gas given off by the liquid whose corrected volume we have just found from the mass of the gas in the dilatometer up to the tap k_6, we must make allowance for the mass of gas in the dead spaces of the narrow capillary, of the small portion d_{f3}, and of the steel capillary d_g that connects the glass capillary with the tap k_6.

The temperatures of the various parts of the narrow glass capillary depend upon the lèvel of the liquid in the bath. Taking this into account they were taken from isotherm measurements, particularly from those given in Comm. N°. 97*a*.

The pressures used in the various experiments were always those of the saturated vapour; for the greater part of the measurements they were found in the manner indicated in § 4.. For temperatures at which the density of the saturated vapour is sufficiently small to be calculated, vapour pressures were found by interpolation from the measurements just mentioned and from the earlier determinations of Comm. N°. 107*a*.

Seeing that oxygen isotherms have not yet been determined for low temperatures the densities in the various parts of the dead space were obtained by calculation, starting from the mean reduced equation of state VII, 1 (Suppl. N°. 19, pp. 17 and 18) given by equation III of Comm. N°. 74 by omitting the terms succeeding $\mathfrak{C}$ and taking account of note 1, Comm. N°. 97*a* p. 24.

In this we put

$$t_k = -118^\circ.8, \qquad p_k = 50.8$$

$$T = t + 273{,}09 \qquad \mathfrak{B} = \frac{B_A}{T_k^2} p_k \, \frac{1}{A^2_{A_0}}, \qquad \mathfrak{C} = \frac{C_A}{T_k^3} p_k^2 \, \frac{1}{A_{A_0}^3}$$

$$A_{A_0} = 1 - (B_{A_0} + C_{A_0} \ldots .)$$

in which A_{A_0}, B_{A_0} .... are the values of A_A, B_A ..... at 0° C.,

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[1]) Mr. de Haas, was kind enough to undertake this calculation for which we wish to record our thanks to him.

$$A_A = (1 + \alpha_{Av} t)\, A_{A_0}\ , \qquad \alpha_{Av} = 0.0036618$$

$$pv_A = A_A + \frac{B_A}{v_A} + \frac{C_A}{{v_A}^2} + \ldots$$

(Comm. N°. 71). Since the question is one of calculation of density at a given pressure the last equation is transformed to

$$pv_A = A_A + B^{(p)} p + C^{(p)} p^2 + D^{(p)} p^3 + \ldots .$$

in which

$$B^{(p)} = \frac{B_A}{A_A}\ , \quad C^{(p)} = \frac{C_A A_A - {B_A}^2}{{A_A}^3}\ , \quad D^{(p)} = \frac{2{B_A}^3 - 3A_A B_A C_A}{{A_A}^5}$$

(cf. Comm. N°. 92, II, p. 18 and N°. 109, p. 7).

In exactly the same way densities at ordinary temperatures may be obtained from the isotherms of Comm. N°. 78. These do not allow the proper evaluation of C_A in the equation given above; on the other hand as is shown in Comm. N°. 71 AMAGAT's isotherms are uncertain as far as B_A is concerned. We therefore take the value of C_A from VII. 1 and subsequently B_A from the isotherms of Comm. N°. 78.

From VII. 1 we get

		B_A	C_A
at	0° C.	$-0.82164 \,.\, 10^{-3}$	$2.1255 \,.\, 10^{-6}$
	15.°6 ,,	$-0.70050 \,.\, 10^{-3}$	$2.1221 \,.\, 10^{-6}$
	20.°0 ,,	$-0.66747 \,.\, 10^{-3}$	$2.1238 \,.\, 10^{-6}$

and from the individual isotherms (Comm. N°. 71 p. 10):

		B_A	C_A
at	0° C.	$-0.9295 \,.\, 10^{-3}$	$2.2931 \,.\, 10^{-6}$
	15.°6 ,,	$-0.7828 \,.\, 10^{-3}$	$2.1925 \,.\, 10^{-6}$

values which do not differ much from those deduced from VII. 1.

Limiting ourselves to the lowest pressures so that the term in C is at the most 10°/₀ of that in B we get from the isotherms of Comm. N°. 78.

		B_A
at	0° C.	$-1.02843 \,.\, 10^{-3}$
	15°.6 ,,	$-0.86388 \,.\, 10^{-3}$
	20° ,,	$-0.87466 \,.\, 10^{-3}$,

and these values are contained in the formula

$$10^3 \,.\, B_A = -1{,}02843 + 0{,}008942\, t.$$

$$A_{A_0} = 1{,}00103$$

This formula was also used for the calibration of the steel capillary

$k_8 - \alpha$ with high pressure oxygen using the auxiliary compressor and the volumenometer.

The equation that is necessary for the reduction of the volume of a quantity of gas measured in c.c. in the volumenometer at a certain pressure and temperature to the normal volume N (at 0°C. and 760 mm.) of that quantity expressed in c.c. may also be obtained from the equation for ordinary temperature. One can easily see from the numbers given above that in these circumstances $C^{(v)}$ is negligible, so that

$$N = \frac{pV}{A_{A_0}(1+\alpha_{AV}t)(1+B^{(p)}p)},$$

for which all the data have been found above. Let us use it to determine the pressure coefficient for oxygen between 0°C. and 20°C. and for a pressure of 1 atm. at 0° C. We get 0.0036746 a number that agrees well with that given by JOLLY[1]).

For the normal density of oxygen we have taken the mean of the values[2]) given by LEDUC, RAYLEIGH, and MORLEY: 0,00142876, 0,00142905, and 0,00142900, viz: 0,00142894.

For the corrections that are applied in the calculation of the volumenometric measurements which give p, V, t, we may refer to the Communications already quoted N°. 84, 88, 92 and to the Communication that we mentioned in § 3 as soon to appear. The accuracy of those measurements is greater than that which we were able to reach with our dilatometer so that the mass data may be taken as certain. As an example we give the following results obtained by each of us measuring the same mass twice:

11 Nov.	1.74448	
12 ,,	1.74432	
		1.74440
11 ,,	1.74450	
12 ,,	1.74449	
		1.74449
		1.74444.

Hence we can be pretty certain of an accuracy of 1 in 4000 in the mass.

To get an idea of the accuracy with which equilibrium to which the measured quantity referred was actually realised,

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[1]) MAKOWER and NOBLE's measurements are doubtful. They give $\alpha = 0.0036655$ for $p = 0$ instead of 0.0036618, a value that is certainly too high.

[2]) DANIEL BERTHELOT, Ztschr. f. Electrochem. 1904 p. 621.

after equilibrium had been reached in our experiment on the density of the vapour and the tap k_8 had been closed we altered the temperature of the cryostat slightly until the liquid phase first disappeared and then reappeared in the appendix. We found that a temperature change of $^1/_{50}$ to $^1/_{20}$ of a degree was sufficient to cause the liquid phase to disappear completely. The absolute values of the temperatures are accurate to about $^1/_{20}$th of a degree except in one case (— 210° C.) in which, owing to unfavourable circumstances, the accuracy attained was $^1/_5$th of a degree.

§ 6. *Results.* For ϱ_{liq} the density of the liquid oxygen, for ϱ_{vap} the density of the saturated vapour with which it is in equilibrium at the same temperature, and for $D_\zeta = \frac{1}{2}(\varrho_{liq} + \varrho_{vap})$ the ordinate of the diameter we obtained the following values:

t	ϱ_{liq}	ϱ_{vap}	$D_{\zeta\,(obs.)}$	$D_{\zeta\,(cal)}$	$O - C$
— 210°.4 C.	1.2746	0.0001	0.6373	0.6373	0
— 182.0	1.1415	0.0051	0.5733	0.5730	+ 0.0003
— 154.51	0.9758	0.0385	0.5072	0.5107	— 0.0035
— 140.2	0.8742	0.0805	0.4773	0.4783	— 0.0010
— 129.9	0.7781	0.1320	0.4550	0.4550	0.0000
— 123.3	0.6779	0.2022	0.4400	0.4400	0
— 120.4	0.6032	0.2701	0.4366	0.4335	+ 0.0031

The calculated values of the diameter are taken from the equation.

$$D_{\zeta\,cal} = 0.1608 - 0.002265\, t$$

The results are plotted on Plate III.

By putting t equal to the critical temperature — 118.°8 C. a value $\varrho_k = 0.4299$ is found for the critical density. This value compared with the value of ϱ_{liq} at — 210.°C., is in good agreement with the law of the *third of the density.*

From

$$b_d = -0{,}002265$$

the absolute value of the slope of the diameter $D_\zeta = a_d + b_d\, T$, taking $T_k = 273.1 - 118.8$ the reduced slope is found to be

$$\mathfrak{b}_d = \frac{T_k b_d}{\varrho_k} = -0{,}813.$$

The deviation at — 154°.5 C., the density of the vapour being

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[1] E. Mathias. Remarques sur le Théorème des états correspondants. Ann. de Toulouse t. V. 1891.

obtained from the mean equation of state (see § 5), is probably due to an error in the experiment; we have been able to trace a probable cause that would afford a complete explanation of its occurrence. As for the temperature $-120^\circ.4$ C., it is in the neighbourhood of the critical state and ought not, therefore, to influence our conclusions.

We come, therefore, to the conclusion that the diameter for oxygen is to a high degree of approximation rectilinear. The liquid densities differ very little from the values given by DEWAR's experiments and by those of BALY and DONNAN. It should also be noted that the values we have found for b_d, V_d, and ϱ_k are almost identical with the values

$$b_d = -0,002264,\quad V_d = -0.800,\quad \varrho_k = 0.4387,$$

deduced by one of us (E. M.) from WROBLEWSKI's measurements at low temperatures.

It may be noticed in conclusion that the critical virial quotient was found to be

$$K_4 = \frac{RT_k}{p_k v_k} = 3,346$$

a value that is smaller than those for all normal substances of higher critical temperature (see KUENEN, Zustandsgleichung p. 60) which run from 3.4 to 3.9; hence oxygen approximates more than any of these to the value given by VAN DER WAALS's equation of state, 2.67.

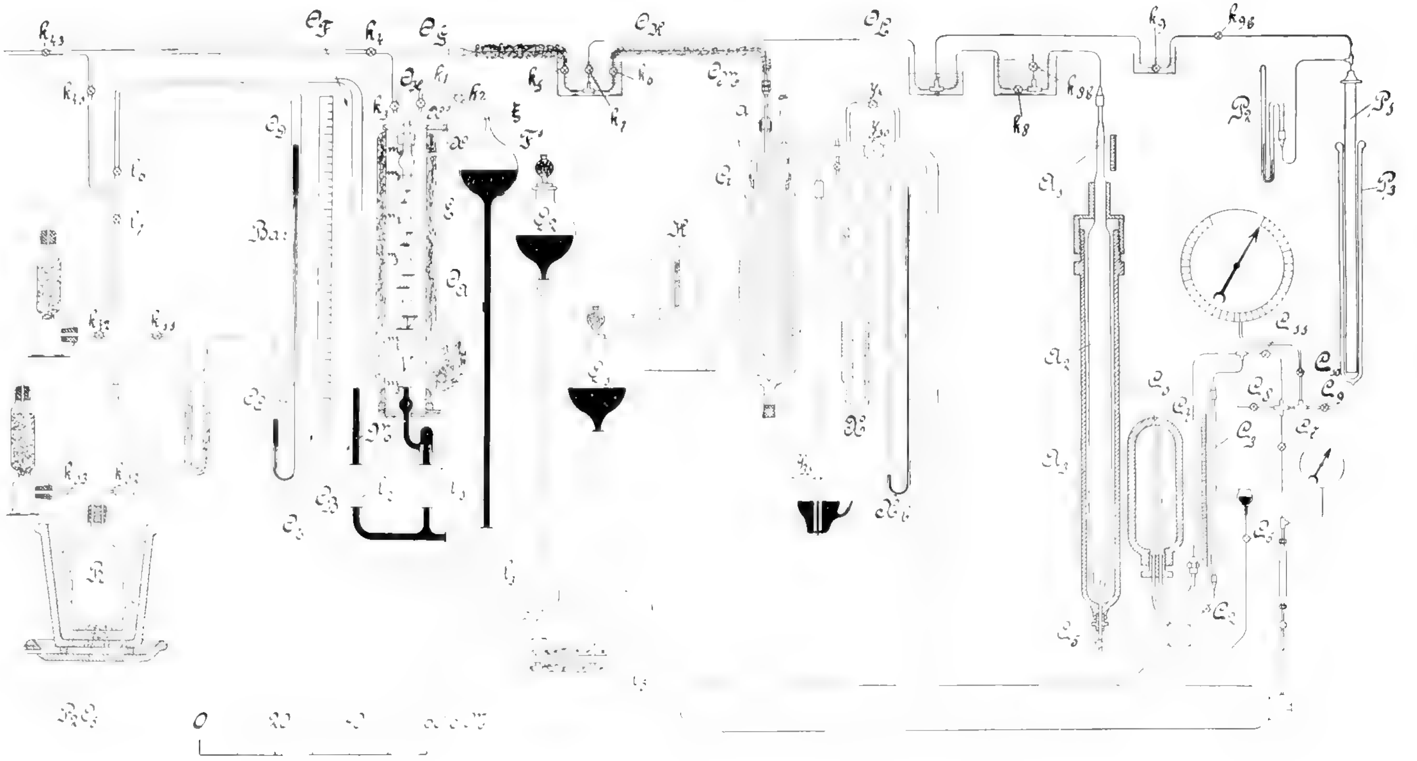
Chemistry. — *"The nitration of aniline and of some anilides".* By Prof. A. F. HOLLEMAN, J. C. HARTOGS and T. VAN DER LINDEN.

(This communication will not be published in these Proceedings).

(March 23, 1911).

E. MATHIAS and H. KAMERLINGH ONNES. „The rectilinear diameter for oxygen”.

Pl. I.



Prof. Ph. Kohnstamm and Dr. J. Timmermans:

ADDENDUM.

Since the publication of the original paper (see These Proceedings p. 865) we have determined the following:

Boiling point line of isopentane + nitrobenzene.
Temperature of the critical end-point 32.°1.

Concentration				
x	weight of nitrobenzene to 100 parts of mixture	Boiling point	$\frac{dT}{dx}$	$\frac{dT}{dc}$
0.0	0.000	27°.95	29°.3	0°.176
6.8	0.041	29.15	15.9	0.101
13.2	0.082	29.80	6.7	0.046
24.15	0.157	30.30	2.5	0.019
32.1	0.217	30.45	0.0	0.0
39.0	0.273	30.45	0.0	0.0
58.7	0.454	30.45	7.8	0.080
68.15	0.556	31.25	35.8	0.43
73.85	0.623	33.65	470.0	6.8
100.0	1.000	210.85		

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday March 25, 1911.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 25 Maart 1911, Dl. XIX).

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Physiology. — "*Experimental researches on the analogy between swelling (imbibition) and mixing.*" By J. R. Katz. (Communicated by Prof. C. A. Pekelharing).

(Communicated in the meeting of November 26, 1910).

Among the chapters of General Physiological Chemistry there are few which invite to a further study so much as that on swelling. Partly, because so little is known and understood as yet, about this phenomenon already noticed in ancient times, and also because the knowledge of the laws of swelling and the explanation of the imbibition process prove to be of fundamental significance for physiology, pharmacodynamics and preparative physiological chemistry.

For physiology, because the protoplasm and the cellnucleus (which together form the material substratum which is the seat of life) are built up of a system of imbibing bodies and interposed liquids. Many phenomena of life are associated with the motion of water from those solid bodies to the surrounding liquids (or reversedly) and between those bodies mutually. And it has often been tried to attribute to those water displacements a fundamental significance by making them the basis of an explanation of those processes of life. So for instance, in the theory of the muscular contraction of Engelmann[1], who, guided by extended *morphological* researches as to the changes in the contracting muscle, has tried to demonstrate that the transformator by which the chemical energy of the metabolism in the muscle is converted into mechanical power, consists of a system of imbibing bodies and acts by displacement of water between these bodies mutually. "During the contraction the anisotropous layer swells owing to imbibition of water which it derives from the isotropous layers with which it comes into contact. Each anisotropous layer is, so far as the muscular fibre extends, provided at both sides with a layer from which it can draw water, which it can again return when the contraction ceases." [2]

By means of this hypothesis many facts which are noticed in the contraction of the muscle are explained qualitatively, and Engelmann demonstrated by his well-known violin string pattern that the theory can also account, more or less, for the form of the line which

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[1] Summarized in his Croonian Lecture, Proc. Roy. Soc. vol **57**, p. 411-433.

[2] Pekelharing (Voordrachten over Weefselleer, p 398) thus summarises Engelmann's views.

represents how the length of a contracting muscle depends on the time. But this is not enough. The success with which WERTHEIM SALOMONSON, HOORWEG and others have been able to represent the curves experimentally obtained by formulae relatively so simple, points to the fact that the theory, if really satisfactory, will have to lead to similar formulae. But in order to work out the theory so far, it is necessary, however to know the quantitative laws of swelling; to know on what it depends whether in a system of imbibing bodies the water will, or will not, be displaced, and according to what formulae the different properties of a swelling substance depend on the degree of imbibition.

For pharmacodynamics. A drug absorbed in the blood, when it has been administered in small doses, frequently affects the function of one organ only and this is explained by assuming that a substance causes *ceteris paribus* a more drastic change in the life processes of an organ when it is present in a greater concentration and by the fact that different organs absorb very different quantities of a drug from the same solution (blood for instance). This creates a connection between elective action and relative strength of the imbibition in different kinds of cells [1]), which has proved fruitful as a working hypothesis. Of late years a commencement has been made to work out this theory also quantitatively. The elegant researches of W. STRAUB on the action of veratrine on the Aplysia heart and the immunochemical theories of ARRHENIUS may be cited as examples. In all these calculations it is assumed that the so-called division rule of NERNST (a sequel of VAN 'T HOFF's laws of dilute solutions) is also available for the imbibition of dissolved substances in swelling bodies. However interesting and plausible these applications may appear, it admits in my opinion of serious doubt whether in all these cases the laws of dilute solutions have been used within their proper limits. [2]) If they have not, the argument would, in some cases, not rest on a sufficiently firm basis, notwithstanding its apparent solidity.

This difficult question can only be answered when a thorough knowledge of quantitative laws and an explanation of the swelling process is obtained.

For preparative physiological chemistry. All polysaccharides and albuminous substances undergo swelling in water and it is greatly in consequence of this property that the chemistry of these substances

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[1]) Compare H. J. HAMBURGER, De physische scheikunde en hare beteekenis voor de geneeskundige wetenschappen, 1901, pag. 7, 20.

[2]) I will refer to this important question in detail, later.

is of such a peculiar character. The criticism of the methods for the purification of these substances, the characteristics of their purity, the question whether the water contained in imbibing crystals may be put — at least in part — on a par with the water of crystallisation of inorganic salts (as pretended by HOPPE SEYLER[1]) and others in the case of oxyhaemoglobin crystals), the question whether the molecular weight of the imbibing substances can be determined from the decrease of their water vapour pressure, and so many other questions of that kind, are problems which the physiological chemist has, so to speak, to face daily, but which cannot be treated fully before the quantitative laws of swelling, and a due explanation of the same shall have been discovered.

But relatively little being known of this matter at that time, I have been engaged since the summer of 1904 upon an extensive research in order to get a better insight into these quantitative laws and their explanation. Very soon, some remarkable regularities and analogies were brought to light. I thought it desirable, however, not to publish these results before they had been confirmed so repeatedly that they could not be looked upon as being merely accidental.

In October 1906 I had found the analogy now described in this first publication, and communicated the same to my teachers Profs. H. W. BAKHUIS ROOZEBOOM and A. SMITS. In this paper I will give only a brief and partial account of the experiments carried out. For experimental details and the literature on the subject the more extended publication which will appear shortly, should be consulted.

Short description of the phenomena of swelling.

Before describing the researches on imbibition it appears to me desirable to point out, briefly, which phenomenon I have studied, from which similar, but yet different, phenomena it must be distinguished, and in which substances it is met with. This seems to me particularly desirable because these facts are sometimes mentioned in physics and chemistry under another name.

By *swelling* or *imbibition power*[2]) the biologists understand the

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[1]) Cf. SCHÄFER'S Textbook of Physiology, I. p. 205 (1898).

[2]) The majority of investigators understand by imbibition power the same as swelling power. REINKE (HANSTEIN'S Botan. Abh. IV, p. 2 and 3) differs from this view; his idea of imbibition power includes porosity as well. I do not

property of some solid substances, which under the most powerful microscope do not show visible pores, to occlude liquids between their smallest particles. If they are examined again after the absorption of the liquid it is impossible to distinguish the separate particles of the liquid and the solid substance even when using the most powerful lenses.

During this absorption of liquid the smallest particles of the solid body are separated from each other by the penetrating molecules of water. Reinke has called this increase of the distance between the particles the *increase of disgregation* of the solid substance. Because those particles get at a greater distance from each other, the volume and length measurements of the solid body suffer an increase[1]; hence the name "swelling". At the same time the cohesion between the particles of the solid substance appears to have much decreased[2]).

On the other hand we may expect that there will exist a great affinity between the water and the solid body if this is able to overcome the so powerful cohesion of the solid substance. This suspicion is confirmed; during the swelling a considerable amount of heat is liberated[3]) and an important contraction of volume takes place, in other words, the volume of the swollen body is considerably smaller than the sum of the volume of the solid substance and that of the imbibed water.

On drying, the swollen bodies can again part with the liquid absorbed; if this takes place slowly the homogeneity is retained. The phenomenon is — at least in the main — reversible.

Some swelling bodies, such as casein, wood, etc. when placed in contact with saturated water vapour absorb only a limited quantity of water and a so-called maximum of imbibition is reached (bodies of limited imbibition power); others such as gum arabic and peptone take up an unlimited amount of water causing them to become more and more fluid so that they, finally, get converted into a liquid mixture of water and imbibing substance (bodies of unlimited imbibition power).

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agree with him. The above definition is borrowed from Hugo de Vries, Leerboek der Plantenphysiologie, 4e Ed, p. 149-150 and from H. A. Lorentz, Leerboek der Natuurkunde, 2e Ed., Vol. I, p. 419.

[1]) Sometimes very considerably; peas double in size, Irish moss (Chondrus crispus) swells to treble its size. (Hugo de Vries, loc. cit. 4e Ed. p. 150).

[2]) Reinke (loc. cit. p. 31) found that if air-dry Laminaria absorbs 300 % of water its ductility increases sixty fold while the breaking strain falls to one-tenth of its value.

[3]) If amylum tritici, dried at 90°, is stirred with its own weight of water, the temperature rises more than 10° (Nägeli, Theorie der Gährung, (1879) p. 133-134)

On no account must imbibition be confounded with the porosity of some solid substances such as bricks, gypsum, and others which by surface adsorption and capillarity can absorb liquids in *visible preformed pores.* NÄGELI [1]) in 1858 already pointed out the difference between these two properties. In the porous absorption of water, the particles of the solid body are not forcibly separated; there is no increase of disgration, therefore no increase in size and no loss of cohesion. Typical imbibition is, therefore, sharply distinguished from typical porosity.

It is principally among the products derived from living organisms that the imbibition power is often, in fact almost regularly, met with. Not only nearly all such substances (cellular walls, fibres, flour, wood, whalebone, leather, horn, etc.) possess swelling power but the pure physiologico-chemical compounds derived therefrom appear to possess these properties also.

Yet, the imbibition power is not limited exclusively to substances of vital origin. It is also observed in synthetically prepared and in inorganic substances; as instances, I cite copper ferrocyanide, clay, tricalcium phosphate, and silicic acid.

The solid substances capable of imbibing water [2]) are amorphous, crystalline, or organised. The majority is amorphous that is to say, possesses no visible regular arrangement of particles [3]).

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[1]) Die Stärkekörner, Zürich, F. SCHULTHESS, 1858, p. 332, 343.

[2]) Substances are known which absorb liquids other than water; caoutchouc, for instance, imbibes ether, oil, pyridin, and even liquid carbon dioxide; nitrocellulose swells in alcohol-ether mixtures and in nitroglycerol It is possible that the imbibition laws in some of these organic liquids are more simple than in the case of water because this is partly associated to complex molecules (perhaps H_4O_2) and because the association degree of the imbibed water must necessarily alter. For physiological purposes the behaviour with water is, for the moment, the most important matter and therefore, I will limit myself to this.

On the imbibition in aqueous solutions of salts, whereon HOFMEISTER, SPIRO, PAULI, WO OSTWALD, H. FISCHER among others have made interesting experiments, I will deal when I have dwelt on the imbibition power in pure water.

[3]) In practice it is sometimes difficult to decide whether an imbibing substance is amorphous or crystalline. For, the external form of a typical crystal, with its regular limitation by flat planes, may be wanting without the substance ceasing to be crystalline. On the other hand an amorphous swelling body may, owing to tensions on drying, exhibit optical phenomena which remind one strongly of those by a crystalline substance (compare the experiments of AMBRONN, Ber. der Sächs. Gesellsch. d. Wiss. 1891 p. 349). The mere presence of anisotropism is, therefore, not in the least sufficient to prove a substance to be crystalline. So long as crystallography does not throw more light on this obscure question, I think it best to look on imbibing substance as amorphous, unless there is sufficient evidence to call it crystalline or organised.

The existence of *swelling crystals* is in my opinion one of the most remarkable facts which have become known in the study of the imbibition phenomena. It is certainly very striking that a typical crystal with its characteristic optical phenomena and corresponding cleavage planes can imbibe water without loss of its crystal nature and its homogeneity. But it creates still more surprise to notice that *all* known crystals of polysaccharides or albuminous bodies undergo swelling in water. It does not seem easy to explain how a crystal can swell while preserving its crystal nature. But no theory of imbibition can be called satisfactory unless it can fully account for this fact. The swelling crystals appear to me the touchstone of the imbibition theories.

Next to the amorphous and the crystalline swelling bodies, organic nature yields quite a series of products such as starch granules, bark fibres, woody fibres etc. which possess no crystal form, but instead, an arrangement of particles with corresponding optical phenomena and cleavage planes [1]). Some investigators have felt inclined to look upon these so-called organised bodies [2]) as crystals with atypic limitation planes; others as amorphous substances wherein tensions occur. Neither of these two ideas seems to me quite satisfactory. And, provisionally, I think the best thing is to look upon the organised matters as a separate group, being more or less a medium between the amorphous and crystalline substances [3]).

The analogy between swelling and mixing.

The fact that a certain analogy exists between the processes of swelling and mixing had been already observed by BERTHOLLET in 1803. In his "Essai de Statique Chimique" he explains both processes by the same mechanism [4]). The physiologists who have worked in the third quarter of the nineteenth century on the subject of swelling — I only mention, CARL LUDWIG, NÄGELI, REINKE also show in their publications in various places that they have noticed the existence of that analogy.

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[1]) Illustrations are given in each test-book of botany.

[2]) Amongst the organised bodies must also be reckoned the arisotropous layers of grained muscles.

[3]) Whether it is more in particular amongst the organised bodies that the much looked for continuity between amorphous and crystalline aggregation condition is perhaps to be found, is a question which I can only propound, but not answer. Cf. also the facts mentioned by W. PFEFFER, Pflanzenphysiologie I. p. 69—70.

[4]) Compare Vol. I, p. 34 and 38.

In order to get a clear idea of the analogy one should imagine a space containing water vapour in which are placed near each other a globular shaped imbibing substance (for instance a piece of sharply dried gelatin or gum arabic) and a drop of a liquid which is not readily volatile but easily mixes with water (for instance sulphuric acid or glycerin). Both now appear to be hygroscopic, both absorb water without loss of homogeneity; both *increase in size* because the volume of the mixture like that of the swollen substance is, approximately, additive and because the substance remains homogeneous during the water absorption. By this dilation without loss of homogeneity [1]) the particles of the swelling body, like those of the sulphuric acid, or glycerin get further removed from each other: in both the disgregation, as REINKE calls it, of these particles increases. If the two phenomena are compared more closely, it appears in both cases that the water absorption is accompanied by a considerable evolution of heat and a decided contraction of volume. There is only one point of difference between the two phenomena; the swelling body possesses the solid aggregation condition and retains the same during the absorption of the water whereas the miscible substance is liquid and remains liquid.

This gulf is, however, more or less bridged over by what is observed in the substances with unlimited imbibition power. If, for instance, powdered gum arabic is allowed to take up moisture, it begins to cake when 30 °/₀ of water has been absorbed, with 40 °/₀ it forms a plastic mass, with 60 °/₀ it is still solid but soft and when 110 °/₀ has been absorbed a watery solution of gum arabic is obtained which becomes less viscous on further dilution. Ovoalbumin, peptone and dextrin behave in the same manner. Here we see how typical swelling substances *gradually* become aqueous mixtures, owing to water absorption. The two phenomena, therefore, not only resemble each other, but must be indeed closely related. Or perhaps even identical?

The older investigators have not dared to assent to the identity,

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[1]) One might perhaps object that the aqueous solution of gum arabic so formed is not a real but a colloidal solution. In the case of substances such as gum arabic, dextrin, and peptone, the difference between real and colloidal solution is but very slight. That this objection is not of great importance is shown by the fact that solutions of substances devoid of colloidal properties such as fructose (which has a low molecular weight and possesses normal values for the lowering of the freezing point and the elevation of the boiling point) are also gradually converted on drying (if crystallisation is prevented) into a solid substance having all the properties of a swelling substance. The sodium salt of glycerol-phosphoric acid behaves similarly.

although they noticed plainly the close relationship. REINKE, who in 1879 discussed[1]) the analogy and observed it more keenly than any one before him, evidently still hesitated — as in fact all his contemporaries would have done — to assume that *miscibility* should exist in the *solid* condition.

But the development of physical chemistry in the last twenty-five years has removed this difficulty. In 1890 VAN 'T HOFF published his celebrated theory of the solid solutions, which shows that miscibility exists in the solid condition just as well as in the liquid state, and the cases have become almost innumerable where this miscibility has been actually observed. In consequence, the difficulty of the older writers has been removed and now, I ask, what can still prevent us from assuming that swelling means mixing[2]), in other words that *when a solid substance swells in water, this depends on the formation of a solid solution of water in the imbibing body*[3]).

Of great significance to the problem of imbibition, seems to me to be TAMMANN's idea[4]) that amorphous solid substances are in many cases nothing but liquids of very great viscosity. TAMMANN showed that all possible liquids, if they are cooled rapidly enough to prevent crystallisation, become *gradually* more and more viscous and are converted, without any discontinuity, into solid amorphous bodies; known instances of this are glass, cane-sugar, glycerin. This view, also warmly defended by BAKHUIS ROOZEBOOM and O. LEHMANN, throws a remarkable light on the fact that the substances of unlimited imbibition power (which are all amorphous), when absorbing water, are converted continuously into aqueous solutions. It leads us to the hypothesis that *amorphous swelling bodies are substances of so great a viscosity that they practically possess the solid aggregation condition, but have still retained their miscibility with water.*

If this hypothesis is correct the swelling of a piece of gelatin and the water absorption of such liquids as sulphuric acid and glycerin

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1) Loc. cit. p. 123—128.

2) The substances of limited imbibition power would then be analogous to those of limited miscibility, those of unlimited imbibition power to those of unlimited miscibility. Limited and unlimited miscibility are not different properties; in substances with a critical mixing point both pass into each other at a change of temperature.

3) Similar hypotheses have been propounded repeatedly by physico-chemists. But they have not worked out this supposition any further, to ascertain whether it can be used as a working hypothesis in the investigation of the quantitative laws of the imbibition power.

4) Compare Zeitschr. f. physikal. Chem., **25**, p. 469—479.

will not only agree qualitatively but the *quantitative laws of the two phenomena will probably be the same.*

Experimental research as to the analogy in the quantitative laws of the two phenomena.

Whatever value one likes to attach to the theory of imbibition advanced, it leads in any case to a thesis which can be controlled experimentally.[1] I have, therefore, instituted a comparative research as to the quantitative laws of imbibition in a number of amorphous swelling bodies and as to the miscibility in a number of comparable miscible substances; as such I have chosen three liquids, which like imbibing bodies are practically non-volatile and can like these absorb large quantities of water, namely sulphuric acid, glycerin and orthophosphoric acid.

In the case of a number of amorphous swelling substances, I determined, experimentally, the quantitative relations according to which the heat of imbibition, the water vapour pressure and the volume contraction depend on the degree of imbibition; the results obtained were represented graphically. In a few cases I could make use of measurements executed by other investigators.

Afterwards, I did the same with the three miscible liquids. For the greater part I could make use here of measurements already carried out by previous investigators for other purposes. But the water vapour pressures of glycerin- and phosphoric acid-mixtures had to be determined by myself and the heat generated on mixing glycerin and water was measured in a series of experiments carried out jointly by myself and Mr. J. J. P. VALETON.

When choosing the swelling substances investigated, I have been careful to avoid unnecessary complications. For instance, such substances as amylum in which layers rich in moisture occur alternately with layers poor in moisture do not seem to me suitable for the research; for each of these layers has a different imbibition power and the phenomenon observed is composed of the sum of numerous elementary phenomena which obey different laws. *A fortiori* intricate products such as peas or Laminaria in which all kinds of elements as cell walls, cell nuclei, starch granules etc. are adjacent to each other are quite out of the question. I have also avoided using sub-

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[1] Experiments of BÜTSCHLI, VAN BEMMELEN among others suggest that in some swelling substances there may be complications, so that the water absorption is not only due to swelling, but partly to capillarity (in preformed pores). In such cases we might expect to find different quantitative laws.

stances such as freshly precipitated silicic acid, or metallic hydroxides wherein probably slow chemical changes take place. For instance the blue cupric hydroxide when in contact with water gradually changes to the black oxide — slowly at the temperature of the room, rapidly at the boiling heat; the brown ferric hydroxide turns red, stannic acid passes into metastannic acid and silicic acid requires an increasing amount of potassium hydroxide to redissolve. Fortunately in the case of albuminous substances and polysaccharides (of which the biologically important substances mostly consist) such complications do not seem to occur; spontaneous peptonisation, which might occur to the mind, does not proceed (at the temperature of the room, and whilst possessing a neutral reaction) with appreciable velocity. In those cases where I have extended my researches to metallic hydroxides etc. I have provisionally, confined myself to substances which by ageing artificially — prolonged heating under water — had been freed as far as possible from this complication. To make quite sure, the samples of the other substances tested were at least one year old.[1])

a. Heat of imbibition and heat of mixing.

The quantity of heat (W) was determined (in gram calories) generated when one gram of dried substance [2]) takes up i gram of water; this quantity I will call the imbibition heat at the imbibition degree i[3]). The substance was put into a glass tube fitted with an india rubber stopper which was then placed in a calorimeter filled with water until there was an equilibrium of heat. By smashing the bottom of the

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[1]) All the substances were investigated in the powdered condition: check experiments had shown that the water adsorption at the surface of the grains of the powder was so small that no hindrance to speak of occurred.

[2]) The name "dry substance" is somewhat vague. I chose as such the substance dried at 110° in vacuo over sulphuric acid. In this manner all the different substances have been obtained as much as possible in a comparable condition.

The substances with the lowest water content with which I have carried out measurements were those dried over sulphuric acid at the temperature of the room; the values for the "dry" substance were obtained by extrapolation. In the case of a few substances which cannot be heated to 110° without decomposition I have determined the water by drying in vacuo over sulphuric acid at the temperature of the room; this is then mentioned separately. Rodewald and his pupils Kattein and Volbehr applied this method of water determination to all substances they investigated. The results of the two methods usually differ $^1/_2$ to 1 %.

[3]) The imbibition degree i therefore is the number of grams of water i absorbed by one gram of dry substance.

tube or by pouring over the content of it the substance was brought into contact with the water and the rise in temperature read off.

The form of the curve indicating how W depends on i has been determined with six substances, of which I only communicate those of *cellulose* (ash-free filters of SCHLEICHER & SCHÜLL) and *casein* (*pur.* HOECHSTER FARBWERKE)[1]. Of the curves published by other investigators, only those of RODEWALD and KATTEIN for *artificially prepared starch granules*[2] and of VOLBEHR for *prepared woody fibres*[3] (as in the determination of crude fibre) seem to me fit for comparison with liquids The other substances investigated by RODEWALD and KATTEIN were species of amylum which, owing to their stratiform structure, form more intricate objects; but there also curves were found which in form agree completely with those of artificial starch granules[4].

On the annexed illustration the curves of these four substances, carefully drawn to scale, are shown. All four make the impression of a hyperbola: this is particularly striking in the case of cellulose and casein[5].

In the case of the other two curves and the cellulose I have questioned whether they may, indeed, be represented by the formula of the hyperbola

$$W = \frac{Ai}{B + i}$$

The subjoined tables show that the agreement is satisfactory[6].

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[1] I beg to offer my sincere thanks to the directors of the Hoechster Farbwerke vorm. MEISTER, LUCIUS and BRÜNING for kindly placing at my disposal the casein required for these experiments.

[2] Zeitschr. f. physikal. Chem. **33**, p. 581.

[3] Untersuchungen über die Quellung der Holzfaser, Inaugural-Dissertation, Kiel (1896) p. 32. VOLBEHR had also observed that the line determined by him had the character of a hyperbola.

[4] Amylum solubile (MERCK) is, for reasons to be stated afterwards, not fit to be compared with liquids; for the rest it presents a line of the same form.

[5] In the case of the other four substances which I have investigated, lines were also obtained which make the impression of hyperbolas.

[6] The deviations are not much greater than the presumable experimental errors.

HEAT OF IMBIBITION OF CELLULOSE.

A = 11.6 B = 0.030 Σ Δ² = 0.59

i	*W* determin.	*W* calculated.	Δ
0.—	0.—	0.—	
0.014	3.5	3.7	+ 0.2
0.041	6.9	6.7	— 0.2
0.054	7.6	7.5	— 0.1
0.074	9.0	8.3	— 0.7
0.261	10.5	10.4	— 0.1

HEAT OF IMBIBITION OF ARTIFICIAL STARCH GRANULES.

dry = dried in vacuo over sulphuric acid at the temperature of the room.

A = 46.65 B = 0.148 Σ Δ² = 1.33

i	*W* determin.	*W* calculated.	Δ
0.—	0.—	0 —	0.0
0.0136	4.1	3.9	— 0.2
0.0236	6.8	6.4	— 0.4
0.0347	8.4	8.9	+ 0.5
0.0424	10.4	10.4	+ 0.0
0.0549	12.2	12.6	+ 0.4
0.0970	18.3	18.4	+ 0.1
0.1218	21.0	21.1	+ 0.1
0.1746	25.3	25.0	— 0.3
0.2403	29.5	28.9	— 0.6
0.3135	32.0	31.7	— 0.3
0.3811	32.8	33.2	+ 0.4

HEAT OF IMBIBITION OF WOODY FIBRES.

(determination of crude fibre).

A = 23.62 B = 0.0895 Σ Δ² = 0.19

i	*W* determin.	*W* calculated	Δ
0.	0.	0.—	
0.0370	6.7	6.9	+ 0.2
0.0697	10.5	10.3	— 0.2
0.0924	11.9	12.0	+ 0.1
0.1269	14.0	13.8	+ 0.2
0.1525	15.0	14.9	+ 0.1
0.1742	15.7	15.6	+ 0.1
0.1964	16.2	16.2	+ 0.0
0.2166	16.5	16.7	+ 0.2

On the same illustration are shown the curves of the heats of mixing for sulphuric acid, glycerin, and orthophosphoric acid (here again the heat of mixing *W* represents the number of gram calories generated when one gram of dry substance takes up *i* gram of water. They exhibit a strong resemblance to the curves of the heat of imbibition.

The two subjoined tables prove indeed that they may be represented by a hyperbola.

HEAT OF MIXING OF SULPHURIC ACID AND WATER.

(THOMSEN).

A = 182.10 B = 0.3303 $\Sigma\Delta^2 = 1.00$

i	*W* determin.	*W* calculated	Δ
0.—	0.—	0.—	
0.1837	65.04	65.07	+0.03
0.3674	96.02	95.88	−0.14
0.5511	113.55	113.86	+0.31
0.9185	133.65	133.93	+0.28
1.653	152.45	151.78	−0.67
3.490	165.74	166.34	+0.60

HEAT OF MIXING OF GLYCERIN AND WATER.

A = 16.40 B = 0.81 $\Sigma\Delta^2 = 0.51$.

i	*W* determin.	*W* calculated	Δ
0.—	0.—	0.—	—
0.1800	3.3	3.0	− 0.3
0.3508	5.1	5.0	− 0.1
0.609	6.9	7.0	+ 0.1
1.234	9.8	9.9	+ 0.1
1.788	11.2	11.3	+ 0.0
3.061	13.0	13.0	+ 0.0
6.170	14.2	14.5	+ 0.3
9.252	14.9	15.1	+ 0.2
12.32	15.3	15.4	+ 0.1
25.35	16.4	15.9	− 0.5

Indeed, THOMSON [1]) was able in 1883 satisfactorily to express his researches on sulphuric acid by means of this empirical formula [2]); and VAN DER WAALS's theory of mixtures leads to the same law. [3])

As will be noticed the analogy between the quantitative laws of swelling and miscibility is striking indeed.

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[1]) Thermochemische Untersuchungen, Vol. III, p. 8.

[2]) E. BOSE, (Physikal. Zeitschr. **6**, p. 548-553) also praises the beautiful results which enabled THOMSON to represent his measurements of the heat of mixing by the hyperbolic formula.

[3]) Continuität des gasförmigen und flüssigen Zustandes, Vol. II, p. 45; as a matter of fact this deduction is made for non-associating substances only.

b. Water vapour pressure.

In the case of forty swelling substances, I have determined the curve according to which the aqueous vapour pressure of the swollen body depends on the degree of imbibition. That pressure has been expressed as fraction (h) of the maximum pressure of water vapour at the same temperature. 1) Such a line which is characteristic for the manner in which the imbibition water is contained in a substance, I will call the *hygrometric line* of the swelling substance. The determinations were carried out according to a method which agrees in the main with the one employed by VAN BEMMELEN 2).

Of eight of these substances, the lines, again drawn carefully to scale, are shown in the illustration. 3) They are *casein, cellulose, gelatin* (the best commercial, after being thoroughly washed with water), *peptone* (amphopeptone prepared by Dr. G. GRÜBLER according to KÜHNE), *gum arabic* (finest commercial, in powder), *serumalbumin* (Albumin aus Blut puriss. Merck, dialysed, filtered and then evaporated at the temperature of the room), *tricalcium phosphate* (calcium phosphoricum tribasicum siccum Merck) and *artificially aged silicic acid* (acumid silicum Merck, heated for half a year under water at 80° C.). The first three and the last two have a limited imbibition power, the fourth, fifth, and sixth an unlimited one; some of these substances belong to the albuminous bodies, others to the polysaccharides, others again to the inorganic compounds. Although substances of a very different nature have, therefore, been used, all lines appeared to possess the same form 4). With small degrees of imbibition the curve

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1) This quotient alters but very little on the rise or fall of the temperature; it is, therefore, advantageous to express the vapour pressure in that manner.

2) The difference with VAN BEMMELEN's method chiefly consisted in the fact that a same portion of the substance did not pass successively through the different equilibria but that different portions of a same substance, after the same preliminary treatment (maximum drying or drenching), came each simultaneously in equilibrium over another sulphuric acid solution. This considerably shortens the time of the experiments otherwise so tedious.

3) A double arrow ↕ on the curve indicates that the equilibrium was approached from two sides, a single arrow ↑ or ↓ that it was reached from one side only and from which one. Check experiments with numerous substances have shown that the form of the lines obtained is the same whether the one or the other method is followed and that the equilibria reached differ but little quantitatively.

4) Apart, of course, from this difference that the curve for $h = 1$ terminates with substances of limited imbibition power in the imbibition maximum, whereas with those of unlimited imbibition power, it takes an asymptotic course. But for the rest the lines of these two groups exhibit no difference.

begins to turn its convex side downwards, gets at a greater i a point of inflection and then turns the concave side downwards, forming a more or less S-shaped line.

So great an agreement with compounds so different chemically is somewhat surprising [2]).

Apparently different from this are some of the results obtained by VAN BEMMELEN. When experimenting with silicic acid freshly precipitated from soluble glass by hydrochloric acid and with ferric hydroxide recently precipitated by alkali from ferric chloride he obtained lines much more complicated, with three points of inflection. If, however, we examine the curves which he obtained from *old* silicic acid [3]) and ferric hydroxide [4]) more closely, they appear to possess the same form as I have found.

In the case of mixtures both experiment and theory lead to the conclusion that the line which indicates how the aqueous vapour pressure depends on i, can have two types which gradually pass into each other. With some substances, for instance with propionic and acetic acids, the concave side is, from the commencement, turned downwards and the point of inflection has disappeared. Glycerin appears to lie exactly on the border line, the curve represented still just shows the point of inflection.

The swelling bodies have, therefore, lines which agree with those of the miscible substances of the first group and bear, indeed, a close resemblance to these.

This analogy goes still further: miscible substances of the first group have a strong heat of mixing and contraction of volume; in those of the second group these properties are mostly but feebly positive or even negative. In all the imbibing substances, as yet investigated, they are strongly positive.

The theory of the mixtures makes one suspect [1]) that the initial

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[2]) Curves of the same form were obtained by TROUTON with flannel and cotton wool, by ORME MASSON and RICHARDS with cotton wool, by LÖWENSTEIN with cupric ferrocyanide, zinc ferrocyanide and silicic acid formed by the action of dilute acid on silicates at the temperature of the room. I myself, have examined more than thirty other swelling substances, among those being the majority of the known physiologico-chemical substances and a few other products such as tannins and soaps; the curves invariably exhibited the S-shaped character

[3]) Zeitschr. f. Anorgan. Chem. 13, p. 354 (fig. 17).

[4]) Zeitschr. f. Anorgan. Chem. 20, p. 207. The line of the jelly which has been kept under water for seven years is meant.

[1]) This follows from the approximative formulae for concentrated mixtures described by NERNST as the formulae of the "ideal concentrated solutions" and also from the expression derived by VAN LAAR from VAN DER WAAL'S theory of

turning downwards of the convex side (and the point of inflection caused thereby) will be the more pronounced in a miscible substance of the group when the so-called "differential heat of imbibition for $i = 0$" is larger, that is to say, the quantity of heat generated when a large quantity of dried substance absorbs one gram of water [2]. With sulphuric acid this character of the vapour pressure line is more strongly pronounced than with phosphoric acid, and with this substance considerably stronger than with glycerin. As will be noticed from the curve, the behaviour of the imbibing bodies lies more or less between that of sulphuric and phosphoric acid. We may, therefore expect as probable that the said heat quantity is greater in sulphuric than in phosphoric acid and much larger than in glycerin, and that in swelling bodies its values lie between those of the substances mentioned first. That such is indeed the case is shown by the subjoined table for the value of this quantity which I have calculated for the different substances from the caloric experiments.

casein	200 cal.	sulphuric acid . .	550 cal.
cellulose	390 ,,	orthophorphoric acid	100 ,,
artificial starch granules . .	320 ,,	glycerin	20 ,,
woody fibres (estimation of crude fibre)	260 ,,		
nuclein (from yeast) . . .	200 ,,		

In the aqueous vapour pressure we find therefore also a resemblance, to in many details, between the quantitative laws of swelling and mixing.

c. Volume contraction.

In the case of three amorphous imbibing substances I have determined to volume contraction c (in cc) which takes place when one gram of dry substance absorbs i grams of water. The method was

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mixtures, for the vapour pressure of mixtures. Particularly in the case of the dilatable substances the formulae of NERNST seem to me to become of great significance. They predict for instance, that if the heat of imbibition is represented by a hyperbola, the hygrometric line must have the S-form, and various particulars of this line which are actually observed. I will refer to this more fully shortly in an article on the Thermodynamics of the Swelling Process.

[2] The differential heat of mixing is calculated from the ordinary heat of mixing according to the formula $w = \frac{dW}{di}$

quite the same as that described by RODEWALD for *amylum tritici*[1]). Petroleumether (b. p. 80°—100° C.) was used as pyknometer-liquid which, as proved by check experiments, is not imbibed by the substances employed. Of the lines determined only those for casein are given; with the other substances I obtained lines of the same shape. I also had reproduced on the illustration the results of RODEWALD with *amylum tritici*, although these experiments are not of great worth for the purpose of comparison with liquids, owing to the presence of layers in the starch granules (in amylum tritici, however, this alternate construction shows but faintly). In both cases the curve exhibits the form of an hyperbola.

In the three miscible substances were found volume contraction lines of the same form [2]); these curves also make the impression of being hyperbolas [3]). In the volume contraction we also find, therefore, the same analogy in the quantitative laws of the two phenomena.

d. Connection between heat of imbibition and contraction of volume.

If the volume contraction c of a swelling substance is divided by the heat of imbibition (W) at the same degree of imbibition, figures are obtained which, in the different imbibing bodies, are in the same order of magnitude. As this relation often changes considerably with the degree of imbibition, I calculated — in order to obtain comparable values — the quotient $\frac{c}{W}$ for very small i's ($i = 0$).

In the three miscible liquids this quotient has also values which agree very well.

What is now particularly striking is that this order of magnitude is the same with miscible and with swelling substances. The subjoined table gives the value of $\left(\frac{c}{W}\right)_{i=0}$:

casein	0.0015	sulphuric acid .	0.0020
amylum tritici	0.0019	orthophosph. acid.	0.0010
woody fibres (crude fibre determ.)	0.0021	glycerin . . .	0.0024

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1) Zeitschr. f. physical. Chem. **24**, 201—202.

2) Calculated from experiments of DOMKE for sulphuric acid (LANDOLT, BÖRNSTEIN, MEYERHOFFER's Tabellen 3e Ed., pg. 328), of SCHIFF for phosphoric acid (Lieb. Ann. **37**, pg. 192); of LENZ for glycerin (LUNGE's Techn. Unters. Meth. III, pg. 160).

3) THOMSON had pointed already out in 1883, that the volume contractions of acetic acid by mixing with water follow a hyperbola.

In swelling, as well as in miscible substances, the quotient, therefore, always lies between 10 and 25×10^{-4}; however different the chemical nature of the substance may be! If the two phenomena are identical in nature, this need not cause astonishment. But how could this agreement in order of magnitude in such greatly different substances be explained if the two phenomena were different in principle?

Summarizing, we see that the laws of imbibition are relatively simple (much simpler than one would have expected after VAN BEMMELEN's experiments) if only care is taken to avoid substances with secondary complications. And it appears that in the four cases where the quantitative laws of the imbibition power of amorphous solid substances were compared with the laws of the miscibility of liquids, a striking analogy exists. *The correctness of the fact that this analogy exists is independent of the correctness of the theory, which has led to the research.* But once found it is a fact with which every theory of swelling will have to reckon.

But whereas it forms a strong confirmation of the theory which proclaims that swelling is in principle the same as mixing, it will be difficult to propose any other theory which can explain unconstrainedly the existence of this analogy.

In a subsequent paper I hope to publish a number of experiments showing that the theory can also account satisfactorily for the imbibition power of swelling crystals.

Physiology. — "*Experimental researches on the analogy between swelling (imbibition) and mixing.* 2nd Communication: *Swelling (imbibing) crystals and mixed crystals*". By J. R. KATZ. (Communicated by Prof. PEKELHARING).

(Communicated in the Meeting of December 24, 1910).

Experiments with swelling (imbibing) crystals.

The question as to how the water of imbibition exists in swelling crystals [1]), has for a long time excited great interest, but a clear insight is not yet obtained. In order that some more light may be thrown on this question it appeared supremely necessary to carry out new

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[1]) Literature reviews on imbibing crystals are found in:
O. LEHMANN, Molekularphysik II, p. 550—553 (1888).
L. MAILLARD, Revue Générale des Sciences 9, p. 608—614 (1898).
FR. N. SCHULZ, Die Krystallisation von Eiweisstoffen, Jena, GUSTAV FISCHER.

experiments. For those executed up to the present, are too few in number to serve as the basis of a fruitful discussion as to the value of the different theories.

In the first place then we want the determination of the line according to which the water vapour pressure of a swollen crystal depends on the degree of imbibition.

In a number of imbibing crystals, therefore, I have determined the form of this line. The water vapour pressure was expressed as a fraction (h) of the maximum pressure of water at the same temperature, the degree of imbibition as the number of grams of water (i) absorbed by one gram of dry substance (hygrometric line).

In the first place I have made experiments with pure carbon monoxide-haemoglobin from horse's blood and from dog's blood, which I prepared according to the method described by PEKELHARING[1]), in his laboratory and under his guidance. The substance investigated consisting of small beautiful rhombic crystals was pressed dry between two plates of unglazed porcelain and then placed in small weighed glass dishes over sulphuric acid-water mixtures of known vapour pressure until an equilibrium was attained; care being taken that the small glass bell-jars in which these experiments were carried out, contained sufficient carbon monoxide to prevent dissociation of the compound. The substance now in equilibrium was, after a spectroscopic test, found to consist of pure carbon monoxide-haemoglobin and not a trace of methaemoglobin could be detected[2]). In each of these portions of the compound the water content was determined by drying in an airbath at 115°. The experiment was made once with carbon monoxide-haemoglobin from dog's blood and twice with that from horse's blood. The results of these last two experimental series agreed very well mutually, a new indication that pure haemoglobin has a composition of relatively great constancy.

The hygrometric lines obtained have been reproduced in the illustration. They exhibit a continuous course, quite different from that of the salts containing water of crystallisation. In the latter, the vapour pressure, when the water content increases, remains constant until the salt has been completely converted into hydrate; if then the substance takes up still more water, another hydrate begins to

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[1]) Voordrachten over Weefselleer, p. 271.

[2]) Analogous experiments were first made with oxyhaemoglobin but did not lead to results of full worth, because during the forming of the equilibrium a portion of this substance was converted into its isomer methaemoglobin. Prof. PEKELHARING then advised me to continue the experiments with carbon monoxide-haemoglobin.

form, the vapour pressure suddenly increases and then remains constant until the salt is completely converted into the second hydrate. Similar sudden increases occur when a third or fourth hydrate is formed. But totally different is the course of the vapour pressure line in the case of carbon monoxide-haemoglobin; no discontinuities occur, the line commences with a nearly horizontal part, turns at first the convex side downwards, acquires a point of inflection and at a still greater degree of imbibition it turns the concave side downwards ¹).

Afterwards I investigated the crystalline albumin from seeds of Cucurbita Pepo, a globulin prepared in large quantities by Dr. G. GRÜBLER in 1881 by extraction with warm solutions of common salt ²). I was enabled to make use of a quantity of the substance prepared by Dr. GRÜBLER personally; it consisted of beautifully formed octahedral crystals and in other respects it also conformed to the description given of it by GRÜBLER.

The method of the vapour pressure determinations in these and further substances was the same as that followed in the case of the amorphous substances. The hygrometric line is shown in the illustration; it agrees in form with that of the carbon monoxide-haemoglobin.

As a third example I investigated the crystalline Bence Jones's albumose, which Miss A. GRUTTERINK and Miss WEEVERS DE GRAAFF have prepared from pathological human urine ³). The substance used for the research was kindly handed over to me by Miss GRUTTERINK; she had freed it, by washing with water and decantation, as much as possible from ammonium sulphate. The substance consisted of beautiful prismatic, presumably hexagonal crystals. Here also an S-shaped line with a continuous course was obtained (see illustration).

Besides these three albuminous bodies, I also investigated a crys-

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¹) HOPPE SEYLER and others (Schäfer's Textbook of Physiology I, p. 205) are of opinion that a fundamental difference may be made between the water of imbibition which is given off on drying at the temperature of the room and that retained until the temperature reaches 115° C. The latter, represented in the hygrometric line by the almost horizontal part, is called by them the "water of crystallisation" of the substance. In my opinion there is no sufficient reason for such a fundamental distinction between the parts of a same continuous line. Moreover, the same phenomenon is found in amorphous imbibing substances (even in cases of unlimited imbibition power, such as serumalbumin and gum arabic) which are presumably liquids of very great viscosity and where there can be no question of water of crystallisation. Even in these cases the substance dried at room temperature still loses a little water when heated to 110°.

²) Journ. f. prakt. Ch. **23**, p. 97—137.

³) Zeitschr. f. physiol. Chem. **34**, p. 393—407.

talline polysaccharide, amylodextrin, which had been prepared in two different ways. The first specimen was made according to the method proposed by NÄGELI[1]) and agreed entirely with the description given by that author of the substance; I am indebted for this substance to Prof. H. P. WIJSMAN, who had it prepared for me by one of his students under his supervision. The other sample was made according to the directions given by Prof. ARTHUR MEYER[2]) of Marburg and had been kindly presented to me by that author for these experiments. It still contained a trace of dextrin, but this was too trifling to be able to cause any significant changes in the form of the hygrometric line. As seen in the illustration, in both samples of amylodextrin an S-shaped line having a continuous course was found[3]).

Summarizing: The form of the hygrometric line was determined in the case of three crystaliine albuminous substances and one crystalline polysaccharide. This line had in all cases a continuous course, showed nowhere discontinuities as is the case with inorganic salts containing water of crystallisation, and had in all cases an S-shaped form; the lines of the various substances strongly resembled each other.

And the remarkable fact appeared that the form of the hygrometric line is the same in the case of swelling crystals as in that of imbibing amorphous substances.

Comparison of swelling (imbibing) crystals with mixed crystals.

Let us now ask ourselves whether this behaviour is in harmony with the hypothesis advanced that swelling should depend on the formation of a solid solution of water in the imbibing body.

Solid solutions in the crystalline condition are called mixed crystals. The said theory applied to swelling crystals therefore runs: *Crystals when swelling form mixed crystals with water.*

For our knowledge of mixed crystals we are chiefly indebted to the researches of the physico-chemists during the last twenty-five years. The pioneer work has been carried out chiefly by O. LEHMANN, RETGERS, VAN 'T HOFF and BAKHUIS ROOZEBOOM. And so numerous

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[1]) Lieb. Ann. **173**, p. 218–227 (1874); for the description of the crystals see in particular p. 223. Also compare BROWN and MORRIS Journ Chem. Soc. **55**, p. 449 (1889).

[2]) Untersuchungen über die Stärkekörner, Jena 1895.

[3]) I am still engaged upon a crystalline lipoide, protagon, and a crystalline globulin, the edestin from hempseeds. The results will be communicated in the more extensive publication.

has become the number of examples[1]) of substances which together form mixed crystals that one is obliged to include the behaviour of common substances such as quartz, inorganic salts and metals in respect to water — where this miscibility in the solid state appears to occur but rarely — in the cases where this miscibility is so small that it readily escapes observation.

It is characteristic of a mixed crystal that it can take up, or lose, a certain quantity of one of the components (such as water) the crystal remaining homogeneous but also (what is closely connected with this) that according to a continuous line the vapour pressure of that component depends on the composition[2]).

As will be seen, the imbibing crystals behave exactly like mixed crystals and even fall under the definition "mixed crystal" in my opinion. Can this theory, however, also explain swelling, or enlargement by water absorption? RETGERS[3]) showed in 1889 that in the case of mixed crystals the volume of the mixture at the first contact is equal to the sum of the volumes of the components. When applied to the imbibition phenomenon this rule teaches us that when a swelling crystal with a volume of 1 mm.^{3} takes up 1 mm.^{3} of water — as is the case with the crystallised Bence Jones' albumose — the volume of the swollen crystal must be two mm.^{3}; and when the crystal remains homogeneous, all the length measure must necessarily increase in size.

Finally, the question arises: but are there also known other substances, for instance some with a less elevated molecular weight, which form mixed crystals with water? It is chiefly TAMMANN[4]) and his pupil LÖWENSTEIN who have found a series of examples thereof.

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[1]) A collection of a large number of examples is found at G. BRUNI, Ueber feste Lösungen, AHRENS' Sammlung chem. and chem. techn. Vortrage 1901 and F. M. JAEGER, Zeitschr. f. Krystallographie **42**, p. 236—276.

[2]) Usually this criterion is expressed in properties of the melting point line; this, however, is closely connected with the vapour pressure line so that this makes no vital difference.

[3]) NERNST, Theoretische Chemie, 2nd Ed., p. 121.

[4]) Wiedemann's Ann. N. F. **63**, p. 16—22 and Zeitschr. f. physikal. Chem. **27**, p 323—336. TAMMANN looks upon these crystals as solid mixtures of an anhydrous zeolithe group with a chemical combination of that group with water (a hydrate). This explanation is not materially different from the one given here, but is only less general. For every compound is in part dissociated and on the other hand, we have serious reasons for believing that most of the mixtures of water with another substance contain hydrate-molecules. The proof that all the water is present as hydrate-molecules is difficult to furnish and has not been given by TAMMANN. I think, myself, it is safer to call them simply mixed crystals with water.

TAMMANN found the first cases in 1896 in magnesium-platinous cyanide and in a whole group of silicates (zeolithes). LÖWENSTEIN [1]) found in 1909 a series of new examples: neutral oxalates, like those of cerium, thorium, erbium, and lanthanum, strychnine sulphate and basic zirconium oxalate ($Zr(C_2O_4)_2 . 2 Zr(OH)_4 . aq.$). In the course of my investigations on swelling in 1907 I myself found new examples in the flavone derivatives quercetin, quercitrin and sophorin.[2]) Quite a series of examples is therefore, known and by a systematic search this number is certain to increase rapidly [3]).

The hygrometric lines of four of these substances: quercitrin, thorium oxalate, the zeolithe calcium chabasite, and basic zirconium oxalate have been reproduced in the illustration for a comparison of their form with those of the swelling crystals. The straight horizontal initial part is in some of these substances considerably longer, in others such as quercitrin and basic zirconium oxalate of nearly the same order of magnitude as in the swelling crystals, but in principle they have the same form: an S-shaped line which commences with an almost horizontal part, turns the convex side downwards, then gets a point of inflection and — at a still larger water content — turns the concave side downwards [4]).

The behaviour of basic zirconium oxalate, which has been investigated by LÖWENSTEIN [5]), is particularly interesting. This substance consists of pyramidal doubly-refracting crystals which are mixed crystals with water and swell to double their size when placed over a 5 $^0/_0$ solution of sulphuric acid under a glass bell jar; for instance a crystal, which, when in equilibrium with a 30 $^0/_0$ sulphuric acid ($h = 0.75$), had a length of 17 scale-divisions, had a length of 32 scale divisions after having been placed over a 5 $^0/_0$ sulphuric

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[1]) Zeitschr. f anorgan. Chemie **63**, p. 69—139.

[2]) These experiments have not yet been published; this will happen shortly.

[3]) Such discoveries have, I think, a great significance for the criticism of the water determinations in preparative, and particularly in organic, chemistry. For, the habit of rounding off the analytical figures obtained in determinations of water of crystallisation to whole figures seems no longer permissible. That the crystal investigated is a hydrate of constant composition cannot be proved by the fact that the analytical figure found is practically a whole number, but only by the determination of the form of the hygrometric line, or that of the melting point line.

[4]) In order to save space in the reproduction, the lines shown in the illustration for calcium chabasite and thorium oxalate are drawn only for values of i larger than 0.20.

[5]) Loc. cit. p. 117.

acid ($h = 0.96$) for three days [1]). Just as SCHIMPER [2]) had found this for the imbibing albumin crystals, the swelling takes place here evenly in all directions so that the crystal form is retained.

Summarizing, we notice that there is so great a resemblance between swelling crystals and mixed crystals that it is difficult to draw a line of limit. If a crystal takes up another component to form a mixed crystal, it will, according to RETGERS' rule, increase in size; if the quantity absorbed is small, the increase in size may readily escape the notice of the observer, if large the crystal is seen to "swell".

The imbibition of crystals is, therefore, explained in an unconstrained manner and without any additional hypothesis by the theory that the swelling depends on the formation of a solid solution. The other theories of swelling met here with great difficulties.

Finally, I just wish to call attention to a fact which appears to me particularly interesting from a physico-chemical point of view, but the details of which are beyond the scope of this communication so that I prefer to devote to it a special article. I allude to the striking resemblance of the quantitative laws of the miscibility in the liquid and in the crystalline condition, at least in regard to the hygrometric lines. Compare, for instance the form of this line in liquid sulphuric acid with that in crystalline basic zirconium oxalate and in crystalline quercitrin (see illustration); the form is quite the same. This explains the analogy found in the form of the hygrometric lines of crystalline and amorphous swelling substances.

The experiments with haemoglobin were carried out in the Physiologo-chemical Laboratory of the University of Utrecht (director prof. C. A. PEKELHARING), those with the other substances in the Physico-chemical Laboratory of the University of Amsterdam (director prof. H. W. BAKHUIS ROOZEBOOM, afterwards prof. A. SMITS).

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[1]) LÖWENSTEIN observed that the crystals then become much softer and, finally, even liquefied. The same thing I have found in haemoglobin and edestin crystals which, at the imbibition maximum are so soft that they amalgamate when pressed between two porcelain plates, whereas in the dry condition they are hard and brittle. This fact is interesting in connection with the nature of liquid crystals: here we notice that crystals which are not liquid acquire this property continuously upon taking up a second component.

[2]) Zeitschr. f. Krystallographie, 1880.

Physiology. — *"On the Influence of Iodoform, Chloroform, and other substances dissoluble in fats, on phagocytosis."* By Prof. HAMBURGER, J. DE HAAN, and Dr. F. BUBANOVIC. [1])

(Communicated in the meeting of January 28, 1911).

For the last 30 years Iodoform has been successfully applied in the treatment of wounds and chronic inflammations. At first it was thought that the favourable effect was based upon an antiseptic action, but the idea was relinquished when it was found that lower organisms amply develop themselves in a medium containing iodine.

Then other hypotheses were suggested which need not be dwelt upon here [2]) They are mainly founded on Iodine being split off.

None of these hypotheses, however, have proved to be generally satisfactory.

For reasons which it is not necessary to state here, we have raised the question whether the favourable effect of Iodoform on local infectious processes might be due, partly at least, to the stimulating effect of this substance on phagocytosis.

The method of investigation adopted corresponded entirely with that we followed when studying in our laboratory the effects of other substances on phagocytosis. [3])

I. EFFECT OF IODOFORM ON PHAGOCYTOSIS.

For this purpose a NaCl-solution of 0.9 °/₀ was shaken with Iodoform powder. Of the saturated Iodoform-solution thus obtained 3 cM^3 were added to 0.2 cM^3 of a suspension of horse leucocytes in NaCl sol. 0.9 °/₀.

At the same time a mixture was prepared of 0.3 cM^3 NaCl sol. 0.9 °/₀ without Iodoform and 0.2 cM^3 of the same leucocyte suspension.

Both mixtures were left to themselves for 1$^1/_2$ hour, exposed for 10 minutes to the influence of 37°, carbon having been previously added, and then cooled down. Finally microscopic preparations were made and it was investigated what percentage of the total amount of white blood corpuscles had taken up carbon. This was also done with suspensions, which instead of 10 minutes, had been in contact with carbon at 37° for 20 minutes, 30 minutes, 1 hour, 1$^1/_2$ hour. Of the many series of experiments made, we subjoin some.

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[1]) More explicit communications will appear elsewhere.

[2]) A discussion of these is found among others in STOKVIS—ZEEHUIZEN's Voordrachten over Geneesmiddelleer. 3rd Ed., 1906, Vol. 1, p. 399 and foll.

[3]) HAMBURGER and HEKMA. Proceedings of June 29th 1907, HAMBURGER u. DE HAAN. Biochem. Zeitschr. **24**. 470, 1910; Cf.also Proceedings of June 9th 1910.

TABLE I.

Effect of Iodoform on phagocytosis.

Time during which the leucocytes were allowed to take up carbon	Percentage of leucocytes having taken up carbon.	
	The leucocytes are in Na Cl 0,9 %	The leucocytes are in a saturated sol. of Iodoform in NaCl 0.9 % (1 to 100.000) [1]
10 minutes	$\frac{173}{424}$[2] $\times 100 = 40,8\%$	$\frac{256}{450} \times 100 = 56,8\%$
20 „	$\frac{185}{342} \times 100 = 54$ „	$\frac{205}{496} \times 100 = 61,4$ „
30 „	$\frac{236}{438} \times 100 = 53,8$ „	$\frac{286}{412} \times 100 = 69,4$ „
1 hour	$\frac{304}{520} \times 100 = 58,5$ „	$\frac{356}{511} \times 100 = 69,9$ „
1½ „	$\frac{402}{597} \times 100 = 67,3$ „	$\frac{381}{543} \times 100 = 70,1$ „

This table shows that after 10 minutes in the pure NaCl-sol. 0.9% 40.8% of the leucocytes had taken up carbon, but in the NaCl sol, containing Iodoform 56.8 %.

After 20 minutes the values are 54 % and 61.4 % respectively. *Hence it appears that Iodoform promotes phagocytosis to a considerable extent.* After 1½ hour the values are: 67.3 % and 70.1 %.

We may infer from this that after that time the extent of phagocytosis has become about equal.

The same facts had been observed before when we studied the effect of Calcium on phagocytosis. As we did then [3] we may also conclude now that the effect of Iodoform is based upon an acceleration of the amoeboid motion, and not upon a greater development of activity (energy) of the phagocytes, rendering cells which under normal circumstances would be too weak to take up particles, capable of doing so by the presence of Iodoform. For if this were the case the phagocytosis would remain considerably lower in the pure NaCl sol. than in the NaCl sol. containing Iodoform. But after 1½ hour

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[1] See page 986.

[2] This means that of the 424 leucocytes counted, 173 had taken up carbon.

[3] Proceedings June 9th 1910.

it has become about equal. Therefore it is only a question of acceleration

As we did formerly, we also investigated in this case to what extent phagocytes which had been left to themselves, exposed for about 18 hours to a somewhat low room-temperature, and which for the greater part seemed to have lost their phagocytarian power as a consequence, could be stimulated again into taking up carbon-particles under the influence of Iodoform.

An answer is supplied by the following experiment.

TABLE II.

Effect of Iodoform on paralyzed phagocytes.

Time during which the leucocytes were allowed to take up carbon particles	Percentage of leucocytes, having taken up carbon	
	The leucocytes are placed in NaCl 0.9$^{0}/_{0}$	The leucocytes have been placed in a solution of Iodoform in NaCl 0,9$^{0}/_{0}$ (1 : 100.000)
$^1/_2$ hour	$\frac{12}{313}\times 100 = 3{,}8\,^{0}/_{0}$	$\frac{202}{440}\times 100 = 45{,}9\,^{0}/_{0}$

It is seen that in a NaCl sol. 0.9 $^{0}/_{0}$ the phagocytarian capacity fell to 3.8$^{0}/_{0}$, but rose again to 45.9$^{0}/_{0}$ when the pure NaCl solution was replaced by one containing Iodoform.

In what concentration does Iodoform exercise a still perceptible influence?

To answer this question Iodoform solutions of different concentrations were prepared. For this purpose we started from a saturated Iodoform solution [1]) diluting it with 5-, 10-, 20- and 50-times the amount of NaCl-solution.

In these solutions the extent of phagocytosis was determined in the usual manner. It need only be observed that the white blood corpuscles were allowed 35 minutes to take up carbon.

The following table III will be clear without further explanation.

This table shows that whilst in NaCl of 0,9 $^{0}/_{0}$ the phagocytosis amounted to 44 $^{0}/_{0}$, it had risen to 59 $^{0}/_{0}$ in the saturated Iodoform solution (0.001 $^{0}/_{0}$ Iodoform or 1 upon to 100.000). This is already a confirmation of the results mentioned in the preceding tables.

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[1]) A saturated solution of Iodoform in NaCl-sol. 0.9 $^{0}/_{0}$ contains about 0.001 $^{0}/_{0}$ CHI_3. We shall revert to this on p. 986.

TABLE III.

Concentration of Iodoform-solution in which the effect on phagocytosis is still perceptible.

Fluids.	Percentage of leucocytes, having taken up carbon.
NaCl 0,9 %[1]	$\frac{171}{388} \times 100 = 44$ %
	$\frac{151}{345} \times 100 = 43,7$ „
1 Iodoform to 100,000 NaCl 0,9 %	$\frac{221}{374} \times 100 = 58,6$ „
	$\frac{226}{377} \times 100 = 59,9$ „
1 Iodoform to 500,000 NaCl 0,9 %	$\frac{228}{371} \times 100 = 61,4$ „
1 Iodoform to 1,000,000 NaCl 0,9 %	$\frac{21}{205} \times 100 = 10,2$ „ ?
1 Iodoform to 2,000,000 NaCl 0,9 %	$\frac{208}{398} \times 100 = 52,2$ „
	$\frac{231}{445} \times 100 = 51,9$ „
1 Iodoform to 5,000,000 NaCl 0,9 % or 1 gr. molecule CHI_3 to 1,900,000 Litres NaCl 0,9 %	$\frac{292}{621} \times 100 = 46,9$ „
	$\frac{176}{372} \times 100 = 47,3$ „

But also in an Iodoform-solution 20 times as weak, a considerable increase is visible, and it may even be perceived in a 50 fold dilution. *In this solution we can no longer distinguish the Iodoform by the smell.*

These results were fully confirmed by experiments with leucocytes which had been left to themselves for about 18 hours. We learn this from the following table.

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[1] We give here parallel experiments which illustrate the exactitude of the method of investigation. As a matter of course parallel experiments have been made in all cases, but it has mostly been thought sufficient to give the average of the results.

TABLE IV.

Concentration of the Iodoform-solution in which the effect on phagocytosis is still perceptible.
The leucocytes had been placed for about 18 hours in Na Cl-sol. of 0.9%.

Fluids.	Percentage of leucocytes, which have taken up carbon.
Na Cl 0,9%	$\frac{55}{485} \times 100 = 11,3\%$
1 Iodoform to 100.000 Na Cl 0.9% (saturated Iodof.-sol.)	$\frac{231}{522} \times 100 = 44,2$ „
1 Iodoform to 500.000 Na Cl 0.9%	$\frac{293}{709} \times 100 = 41,3$
1 Iodoform to 1000.000 Na Cl 0.9%	$\frac{85}{488} \times 100 = 17,4$ „ ?
1 Iodoform to 2000.000 Na Cl 0.9%	$\frac{225}{480} \times 100 = 46,8$ „
1 Iodof. to 5000.000 Na Cl 0.9% (saturated Iodof.-sol. 50 times diluted)	$\frac{156}{488} \times 100 = 31,9$ „

It is seen that in a NaCl-solution of 0,9% the phagocytosis amounts to 11,3%; in the saturated Iodoform-solution 44,2%, and in the 50 fold dilution still 31,9%.

So it appears that in this strong dilution Iodoform is still able to awaken the phagocytes from their slight mobility.

How much Iodoform is found in this fluid?

No data are extant, as far as we know, as to the solubility of Iodoform in water or in NaCl-solution. Therefore we had to make some experiments ourselves. This was done by two methods.

In the first place the clear well filtrated Iodoform-solution was exposed to the light for a considerable time, till the Iodoform smell was no longer observable, and was then treated with concentrated nitric acid. The fluid thus obtained was shaken with chloroform, which caused the iodine to pass into this fluid, and to colour it red. By the side of this NaI-solutions of known concentration were treated with HNO_3 and afterwards with Chloroform.

Finally it was investigated what concentration of a NaI-solution gave the same colour intensity to the chloroform as the Iodoform-solution under examination.

From these experiments it appeared that in the saturated solution of Iodoform in NaCl 0.9% was found 0.001% Iodoform.

The other method which consisted in the Iodoform, split off under the influence of HNO_3, being titrated with the aid of $Na_2S_2O_3$ and $KMnO_4$, gave almost identical results: a concentration of 0.00109%.

So that we may say that even in a concentration of 1 *to* 5.000.000 *or, in other words, in a solution of* 1 *gr. molecule* CHI_3 *to* 1.905.000 *litres water, Iodoform accelerates phagocytosis to a considerable extent.*

The experiments in table IV leave no doubt but that the dilution may be carried on still further.

How does Iodoform effect an acceleration of phagocytosis?

In the first place we proposed to ourselves the question whether it might be perhaps traces of iodine which, though present only as ions, had this stimulating effect. Against this view pleaded already former experiments on the comparative effect of NaCl, NaBr, and NaI, which has shown that the ion of iodine weakens phagocytosis to a considerable extent.[1]

Another objection to this view was furnished by the experiments with an iodoform solution which had been exposed to the light for

TABLE V.

Iodoform solution the composition of which has been modified by the influence of diffuse daylight

Time during which the phagocytes were allowed to take op carbon.	Percentage of leucocytes having taken up carbon.	
	The leucocytes are in NaCl 0.9%	The leucocytes are in a saturated iodoform solution.
10 minutes	$\frac{115}{430} \times 100 = 26,7\%$	$\frac{73}{430} \times 100 = 15,4\%$
20 „	$\frac{121}{474} \times 100 = 27$ „	$\frac{128}{512} \times 100 = 25$ »
30 „	$\frac{189}{465} \times 100 = 40,6$ „	$\frac{128}{512} \times 100 = 34,7$ »
1 hour	$\frac{287}{465} \times 100 = 61,7$ „	$\frac{163}{447} \times 100 = 36,4$ „
1½ „	$\frac{329}{578} \times 100 = 56,9$ „	$\frac{125}{314} \times 100 = 39,8$ »

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[1] HAMBURGER und DE HAAN. Biochem. Zeitschr. **24**, 304, 1910.

a short time. Iodine was not in the solution, but iodine as ions was, probably as HI. For iodine as such could not be shaken out with the help of chloroform only, this however could be done when at the same time HNO_3 was added.

Well then, this iodoform solution, exposed to the light, was not only unable to promote phagocytosis but greatly impeded it.

This may appear from the table V.

We see that in the NaCl-solution containing iodoform the phagocytosis always remains below that in the pure NaCl-solution. We see for instance that after 10 minutes the phagocytosis in a pure NaCl solution amounts to 26.7 %, but in a NaCl-solution containing iodoform only to 15.4 %.

After $1\frac{1}{2}$ hour the values are 56.9% and 39.8%.

The following experiment for which, besides the (old) iodoform-solution which had been exposed to the light, also a fresh one had been taken, confirms the result.

TABLE VI.

Comparison between a fresh iodoform-solution and an old one (one somewhat decomposed by the light).

Time during which the leucocytes were allowed to take up carbon.	Percentage op leucocytes having taken up carbon.	
	The leucocytes are in Na Cl 0,90%	The leucocytes are in a saturated iodoform solution.
10 minutes	$\frac{108}{407} \times 100 = 26,5\,\%$	$\frac{126}{362} \times 100 = 34,8\,\%$
20 ,,	$\frac{129}{365} \times 100 = 35,3$,,	$\frac{219}{442} \times 100 = 49,7$,,
30	$\frac{268}{732} \times 100 = 36,6$,,	$\frac{444}{845} \times 100 = 52,5$,,
		$\frac{91}{342} \times 100 =$ **26,2** ,, (old Iodoformsol.)
1 hour	$\frac{230}{424} \times 100 = 54,2$,,	$\frac{278}{498} \times 100 = 55,8$,,
$1\frac{1}{2}$,,	$\frac{248}{488} \times 100 = 58,8$,,	$\frac{214}{373} \times 100 = 57,3$,,

Our views were moreover confirmed by an experiment, tending to investigate to what extent the phagocytosis could be revived in an 18 hour old leucocyte suspension by the iodoform-solution which had been exposed to the light. In the same experiment the effect of the fresh iodoform-solution was ascertained and also that of chloride of calcium.

At the same time the effect was investigated of a NaCl-solution, containing a slighter amount of the old iodoform, and which had been obtained by diluting the old saturated iodoform solution with double the volume of a NaCl-solution. This experiment we resolved upon with a view to the consideration that if the old iodoform solution contained a noxious substance it would make itself less felt, if this solution were diluted. Under these circumstances, the favourable effect of that iodoform in the solution, which had not been decomposed, would more plainly manifest itself.

TABLE VII.

Effect of fresh and old iodoform-solutions and of $CaCl_2$ on the almost paralyzed leucocytes.

Fluids.	Percentage of leucocytes having taken up carbon.
NaCl 0,9%	$\frac{19}{461} \times 100 = 4{,}1\%$
Fresh saturated solution of Iodoform in NaCl 0,9% (0,001% CHI_3)	$\frac{153}{976} \times 100 = 15{,}6$ »
Old saturated solution of Iodoform in NaCl 0,9%	$\frac{0}{624} \times 100 = 0$ "
1 vol. of the old saturated solution of Iodoform in NaCl 0,9% and 2 vol. NaCl 0,9% (0,0003% CHI_3)	$\frac{76}{594} \times 100 = 12{,}7$ "
NaCl solution 0,9% + 0,05% $CaCl_2$	$\frac{83}{505} \times 100 = 16{,}4$ "

We see from this experiment:

1. that the phagocytosis in the old leucocyte suspension has fallen to about 4%;

2. that the fresh iodoform solution raises the phagocytarian power again to 15.6%, but that

3. in the old iodoform solution the phagocytosis amounts to *nothing*, whereas in a solution, which contains only *one third* of the old iodoform solution, it has increased to 12.7 °/₀.

From these experiments it may be concluded *that not the ion of iodine but Iodoform as such, causes the increased phagocytarian power.*

And now the question suggests itself: how can the favourable effect of iodoform upon the rapidity of the phagocytarian process be explained?

We must obviously think here of *a decrease in the surface-tension which facilitates the amoeboid motions of the protoplasm.*

It is not difficult to account for this decreased surface-tension if we consider that iodoform is soluble in fat substances and that, as may be concluded from numerous investigations, the outer layer of cells consists of a fat substance, a so called lipoid membrane.

Further it is obvious that such a lipoid membrane will grow more flexible after having absorbed iodoform, in other words that the surface tension will decrease, and that consequently the amoeboid motion will be facilitated.

If this interpretation was the correct one, then it might be expected that also other substances, which are soluble in fat, such as chloroform, Benzene, Camphor, would affect phagocytosis in a similar way.

As will appear from the following experiments, this was indeed the case.

2. EFFECT OF CHLOROFORM ON PHAGOCYTOSIS.

It might be expected that, besides an accelerating effect by weakening the outward lipoid layer, chloroform would have a paralyzing effect, opposed to the former, viz. on the protoplasm of the phagocytes.

Therefore various dilutions had to be tried.

Soon it was found that dilutions of 1 to 2000, 1 to 6000 and also 1 to 10000 impair phagocytosis. The following table VIII contains some experiments with weaker dilutions.

From this table it appears that chloroform 1 : 20000 raises the phagocytarian power from 40.9 °/₀ to 50.4 °/₀, further that phagocytosis is considerably increased by chloroform 1 : 100000; there it rises to 60.5 °/₀.

Evidently in the chloroform-solution 1 to 20000 the above mentioned *paralyzing* influence also makes itself felt.

In a dilution of 1 : 500.000 the favourable effect remains, to about he same extent as in 1 : 100.000, and finally in a solution of 1

TABLE VIII.

Concentration of the chloroform-solutions in which the effect upon phagocytes can be observed.

Fluids.	Percentage of leucocytes having taken up carbon.
Na Cl 0,9	$\frac{174}{428} \times 100 = 40,6\,\%$
	$\frac{238}{562} \times 100 = 41,2$,,
chloroform 1 : 20.000	$\frac{244}{480} \times 100 = 50,8$,,
	$\frac{225}{451} \times 100 = 49,8$,,
chloroform 1 : 100.000	$\frac{254}{519} \times 100 = 60,6$,,
	$\frac{382}{455} \times 100 = 60,1$,,
chloroform 1 : 500.000	$\frac{332}{582} \times 100 = 57$,,
	$\frac{219}{370} \times 100 = 59,1$,,
chloroform 1 : 5.000.000	$\frac{379}{868} \times 100 = 43,6$,,
	$\frac{298}{661} \times 100 = 45$,,

chloroform to 5.000.000 NaCl-solution this favourable effect is still visible, it is true, but it is very slight.

The following experiment, made only with solutions of chloroform of 1 to 500.000, but this time with *different* periods of contact between carbon and leucocyte-suspensions confirms what has been said above.

We see from this table that already after 30 minutes the acceleration of phagocytosis, effected by chloroform, has manifested itself at its maximum value. After an hour it still exists, but in a slight degree. The figure 27.5, with the note of interrogation, must be owing to a mistake in the concentration of the solution. Indeed other preparations of the same suspension gave after an action of 45 minutes

TABLE IX.

Influence of Chloroform on phagocytosis.

Time during which the phagocytes were allowed to take up carbon.	Percentage of leucocytes having taken up carbon.	
	The leucocytes are in NaCl 0,9 %.	The leucocytes are in a solution of 1 vol. chlorof to 500,000 NaCl 0,9 %.
10 minutes	$\frac{64}{335} \times 100 = 19$ %	$\frac{100}{386} \times 100 = 25,9$ %
20 „	$\frac{166}{465} \times 100 = 35,7$ „	$\frac{180}{457} \times 100 = 39,3$ „
30 „	$\frac{215}{535} \times 100 = 40,2$ „	$\frac{269}{521} \times 100 = 51,6$ „
45 „	$\frac{330}{722} \times 100 = 45,6$ „	$\frac{106}{385} \times 100 = 27,5$ „ ?
1 hour	$\frac{345}{639} \times 100 = 53,9$ „	$\frac{323}{563} \times 100 = 57,3$ „

likewise much too low a figure. A mistake in counting is therefore not to be thought of.

We now revert to the question, to what extent the leucocytes which have been placed during a night in a solution of NaCl 0.9 °/₀ and which consequently have lost partly or entirely their phagocytarian capacity can be revived again by an addition of chloroform.

To this series of experiments has been added one with Iodoform and one with $CaCl^2$, as we wished to investigate to what extent the stimulating effect of these substances corresponded with that of chloroform.

The table shows that if phagocytes which have been left exposed during one night to a low room-temperature, are acted upon for 1½ hour by Chloroform in a concentration 1 : 500.000, whilst the suspension is afterwards brought into contact for 15 minutes with carbon at 37°, the Phagocytosis will be raised from 8,7 to 11.1 °/₀. *If we give more time to the suspension to take up carbon viz.* 30 *minutes, then the favourable effect of chloroform makes itself more plainly felt, the phagocytosis rising from* 20 *to* 34.2 °/₀. Injurious, however, the effect of chloroform proves to be at a contact of the phagocytes with carbon during 45 minutes; perhaps the cells, which

TABLE X.

Effect of Chloroform on phagocytosis.

The leucocytes have been exposed for about 18 hours to a Na Cl-solution of 0,9%.

Time during which the phagocytes were allowed to take up carbon.	Fluids.	Percentage of the leucocytes having taken up carbon.
15 minutes	Na Cl sol. 0,9%	$\frac{45}{514} \times 100 = 8,7\%$
	1 vol. *Chlorof.* to 560,000 Na Cl sol. 0,9%	$\frac{60}{540} \times 100 = 11,1$ „
30 „	Na Cl sol. 0,9%	$\frac{108}{538} \times 100 = 20$ „
	1 *Chlorof.* to 500,000 Na Cl sol. 0,9%	$\frac{213}{620} \times 100 = 34,2$ „
	Na Cl 0,9% + 0,001% *Iodof.*	$\frac{144}{460} \times 100 = 31,4$ „
	Na Cl 0,9% + 0,05% *CaCl₂*	$\frac{117}{252} \times 100 \quad 46,4$ „
45 „	Na Cl 0,9%	$\frac{179}{609} \times 100 = 29,3$ „
	1 *Chlorof.* to 500,000 NaCl sol of 0,9%	$\frac{57}{228} \times 100 \quad 25$ „

have been weakened already, are further impaired by the longer exposure to 37°, in the presence of chloroform. For this supposition there is a good deal of reason, seeing that longer heating at 37° begins to have an injurious effect *even in a pure NaCl solution.*

As we see from the table the stimulating effect of Iodoform is about equal to that of Chloroform.

To a much more considerable extent than these two, however, Calcium stimulates the phagocytes in these experiments.

3. EFFECT OF BENZENE ON PHAGOCYTOSIS.

Of Benzene (C_6H_6) the following concentrations in a NaCl-solution of 0,9% were made:

1 Vol. to 5000, 1 to 10,000, 1 to 500,000 and 1 to 5,000,000. The fluid acted upon the suspensions during an hour; then they were brought into contact with carbon for 30 minutes at 37°.

TABLE XI.

Concentration of the Benzene-solution in which the effect on phagocytosis is still perceptible.

Fluids.	Percentage of the leucocytes having taken up carbon
NaCl 0,9%	$\frac{266}{642} \times 100 = 41,4\%$
	$\frac{164}{405} \times 100 = 40,5$ »
Benzene 1 : 5000	$\frac{349}{694} \pm 100 = 50,2$ „
	$\frac{282}{576} \times 100 = 48,9$ „
Benzene 1 : 100.000	$\frac{305}{602} \times 100 = 50,6$ „
	$\frac{373}{758} \times 100 = 49,2$ „
Benzene 1 : 500.000	$\frac{276}{478} \times 100 = 57,7$ „
	$\frac{282}{466} \times 100 = 60,5$ „
Benzene 1 : 5000000	$\frac{356}{807} \times 100 = 44,1$ „
	$\frac{168}{412} \times 100 = 40,7$ „

This table leaves no doubt but Benzene too revives phagocytosis. This is visible at a dilution of 1 to 5000, but the effect is found to be much greater at a dilution of 1 to 500,000.

Very likely the cause of this difference will have to be traced to the narcotic influence of benzene. At a dilution of 1 to 5000 OVERTON saw tadpoles pass into narcosis.

These experiments were repeated with leucocytes which had been placed during one night in a NaCl-solution 0,9 %.

Still more clearly than in the preceding table we can observe here the stimulating effect of Benzene. The most favourable proportion is again 1 to 500.000, but a still greater effect is obtained by $CaCl_2$, at least in the concentration given.

TABLE XII.

Effect of Benzene on phagocytosis with leucocytes which had been placed for about 18 hours in a NaCl-solution of 0,9 %.

Fluids.	Percentage of the leucocytes having taken up carbon.
NaCl 0,9 %	$\frac{83}{465} \times 100 = 17,8\%$
	$\frac{75}{410} \times 100 = 18,3$ „
Benzene 1 : 5000	$\frac{106}{257} \times 100 = 29,7$ „
	$\frac{195}{622} \times 100 = 31,3$ „
Benzene 1 : 100,000	$\frac{141}{495} \times 100 = 28,4$ „
	$\frac{198}{854} \times 100 = 23,2$ „
Benzene 1 : 500,000	$\frac{147}{449} \times 100 \quad 32,7$ „
	$\frac{55}{152} \times 100 = 35,5$ „
Benzene 1 : 5,000,000	$\frac{92}{479} \times 100 = 19,2$ „
	$\frac{46}{222} \times 100 = 20,7$ „
$CaCl_2$ 0,05 %	$\frac{153}{410} \times 100 = 37,3$ „

4. EFFECT OF CAMPHOR ON PHAGOCYTOSIS.

We examined a saturated solution [1] of Camphor in NaCl 0.9 % and diluted this solution 5 and 25 times.

In all these fluids the smell was still distinctly noticeable.

After having been brought into contact for an hour at the normal temperature with these fluids, the leucocytes were brought into contact with carbon and left to themselves for 30 minutes at 37°, as usual.

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[1] As we know the solubility in water is very slight.

The following table contains the results of the first series of experiments.

TABLE XIII.

Effect of Champhor on phagocytosis.

Fluids.	Percentage of leucocytes having taken up carbon.
Na Cl 0,9%	$\frac{273}{672} \times 100$ 40,6 %
Saturated Camphor-solution in Na Cl 0,9%	$\frac{284}{540} \times 100$ 52,5 "
Saturated Camphor-solution diluted 5 times	$\frac{278}{550} \times 100$ 50,4 "
Saturated Camphor-solution diluted 25 times.	$\frac{287}{643} \times 100 = 44,6$

It appears from this table that in a saturated Camphor-solution the phagocytosis has increased, likewise when it is diluted with 5 *or* 25 *times its volume of water.*

As in the preceding experiments Camphor was also tried as a means of reviving leucocytes weakened by an 18 hour's stay in a NaCl-solution of 0.9 %.

TABLE XIV.

Effect of Camphor on phagocytosis with leucocytes which had been placed for about 18 hours in a NaCl-solution 0.9%.

Fluids.	Percentage of leucocytes having taken up carbon.
NaCl 0,9%	$\frac{38}{321} \times 100 = 11,8\%$
Saturated Camphor-solution	$\frac{0}{285} \times 100 = 0$ "
Saturated Camphor-solution diluted 5 times.	$\frac{4}{242} \times 100 = 1,7$ "
Saturated Camphor-solution diluted 25 times.	$\frac{13}{292} \times 100 = 4,5$ "
NaCl 0,9% + 0,05% $CaCl_2$	$\frac{132}{308} \times 100 = 42,8$ "

We see from these experiments that the saturated Camphor-solution, instead of reviving the phagocytarian power, has entirely destroyed it. The red blood corpuscles when seen under the microscope have lost their colour and from a number of white ones the contents have passed out.

This it is true could not be observed in the case of the weaker Camphor-solutions, but yet there can be no difficulty in assuming that in these too the phagocytes have suffered, whence no revived phagocytosis took place.

The reason why in the preceding series of experiments the phagocytosis was promoted by Camphor will have to be sought in the fact that in the first case fresh cells were experimented upon, in the second case phagocytes weakened by their long stay in NaCl-solution 0,9 %. Indeed they must have lost ions of Ca and probably also other ions by interchanging them with Na.

That their life has not been destroyed for ever is seen from the fact that an addition of $CaCl_2$ raises the phagocytarian power again to 42,8 %.

There were obvious reasons for repeating the experiment also with *weaker* Camphor-solutions. Therefore we took a saturated Camphor-solution in NaCl 0,9%, diluted it with 10-, 50-, 100- and 500 times its volume of NaCl 0,9%. For the rest the method of experimenting was entirely the same as that followed in the preceding series of experiments.

TABLE XV.

Concentration of the Camphor solution in Na Cl 0,9% at which its effect on phagocytosis is still perceptible.

Fluids.	Percentage of leucocytes having taken up carbon.
Na Cl 0,9%	$\frac{146}{350} \times 100$ 41,7 %
Camphor 1 : 10	$\frac{188}{367} \times 100$ 51,2 ,,
Camphor 1 : 50	$\frac{132}{328} \times 100$ 40,2 ,,
Camphor 1 : 100	$\frac{246}{444} \times 100$ — 55,4 ,,
Camphor 1 : 500	$\frac{196}{399} \times 100$ 49,1 ,,

From this series of experiments it may be concluded that a saturated camphor-solution in a 500-fold dilution still revives phagocytosis.

5. SOME ADDITIONAL REMARKS.

From a survey of the various experiments detailed above it appears that all substances, hitherto experimented upon which dissolve in fat or are soluble in fat, promote phagocytosis to a considerable extent. And we may add *that this was also the case with chloral* (1 *to* 20.000 *and weaker*) *and with turpentine* (1 : 50.000), *which latter result, it may be observed by the way, one will be inclined to connect with the power of turpentine to cause local exsudations, and also with the therapeutic inhalation of turpentine-vapour at tuberculous processes in the respiratory organs, and the stimulating effect of the smell of resin.*

The results we obtained with phagocytes show a remarkable correspondence with what J. LOEB, and afterwards R. S. LILLIE, have observed on the artificial parthenogenesis of eggs [1]).

LOEB *discovered namely that substances dissolving fat have the power to render the parthenogenetic development of eggs possible.*

How can this fact be explained? We may imagine with LOEB that the substance dissolving the lipoid, weakens the egg membrane thus giving rise to the formation of a fertilizing membrane. We think we may safely go one step further, and assume that it is owing to the weakening of the membrane that the movement of the protoplasm, underlying the cell-division, manifests itself. This view is confirmed by the observation of R. S. LILLIE [2]), who saw that also by a short transitory raising of the temperature in eggs of star-fishes a typical fertilizing membrane may be formed, which formation is followed by the development of part of the eggs into larvae. J. LOEB could confirm this as regards the jelly-fish.

There is still more analogy between what has been observed about phagocytes and about eggs. If we allowed more concentrated solutions of Chloroform, Benzene, Camphor, etc. to act upon the phagocytes they caused a decrease in the phagocytosis; in the case of Camphor the cells were even destroyed. Well, LOEB has found that a somewhat protracted action on eggs of fat-dissolving substances causes destruction of these cells, so-called cytolysis.

Consequently the favourable effect which the above-mentioned sub-

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[1]) Cf. a.o. J. LOEB. Die künstliche Parthenogese. Handbuch der Biochemie des Menschen und der Tiere. Band I 1910. p.p. 101 en 102.

[2]) R. S. LILLIE. Journal of Experim. Zoology 5, 1908. 375. (cited from LOEB l.c.).

stances (which are all soluble in fat) have on the mobility of phagocytes and on the development of eggs may be regarded from the same point of view.

But there is still more made clear by the above researches. It is namely a well-known fact that various *narcotics applied in smaller doses have a stimulating effect and paralyze in greater quantities.* Engelmann observed this already many years ago on vibratile cilia and also as regards the nervous system we know of Chloroform, Alcohol, Aether that when first administered, that is to say when they have entered into the nerve-cells in small quantities, they cause excitement, but produce insensibility when a greater amount of the substance has penetrated into the cells. As far as we know this contrast has never been explained, but when viewed in connection with our experiments the phenomenon becomes clear.

Two factors must be distinguished in the working of the narcotic: in the first place it must be dissolved in the lipoid membrane, secondly after having entered into the protoplasm in sufficient quantities it will produce its narcotic effect. But already before the latter has taken place the lipoid membrane has undergone a decrease in its surface tension and the stimulating effect manifests itself. The excitement disappears of course when the protoplasm has been paralysed [1]).

Hence we see that what was observed about phagocytosis deserves ves our attention also from a general point of view. We do not mean to say, and this must be distinctly understood, that all substances dissolving fat have the same effect on various cells; far from it.

In the first place the word "lipoid" is a collective notion, and it may be expected that with different cells the composition of lipoid will be quite different, and also its solubility in one and the same fat-dissolving substance. Secondly not all substances penetrating into cells, dissolve fat or can be mixed with it. Urea may serve as an instance.

And thirdly, it need hardly be observed that the power of a substance to penetrate through the lipoid membrane will by no means determine its further physiological and pharmacological effect. This will be chiefly dependent on the chemical structure of the cell-contents, which are different in the different kinds of cells.

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[1]) The paralyzing effect of narcotics on protoplasm Mansfeld is inclined to attribute to want of oxygen, caused by the decreased permeability of the cellipoids to this gas. (Pfluger's Archiv. **131**, 1910, p. 464.

These remarks have been already confirmed by what we observed. In eggs of sea-urchins and star fishes an artificial membrane-formation could be effected according to investigations of J. LOEB by the addition of slight quantities of digitaline. Yet it was impossible to discover an acceleration of phagocytosis with this substance, nor with Strophantine.

Nevertheless it will be useful to investigate to what extent the facts observed by us hold good for other cells than those mentioned, and also for other substances which dissolve fat.

Hence we are continuing our investigation in this direction, and have already arrived at the preliminary conclusion that the movement of spermatozoa is promoted by diluted solutions of turpentine. We could not effect this by means of Iodoform, perhaps because this substance, in the concentration necessary to increase the mobility, had a deleterious effect upon the living protoplasm.

SUMMARY.

The above investigations have mainly led to the following results:

1. *A saturated solution* (0.001 $^0/_0$) *of Iodoform* in a NaCl-solution of 0,9 $^0/_0$ *is able to accelerate phagocytosis to a very considerable extent.* This favourable effect of Iodoform not only manifests itself in the case of phagocytes which have been obtained from blood a short time before, but also in the case of those which have for the greater part seemingly lost their phagocytarian power, having been placed for a considerable time, e.g. 18 hours, in a NaCl-solution of 0,9 $^0/_0$.

2. The effect of Iodoform is still plainly visible in a fluid containing 1 gramme CHI_3 to 5.000000 cM^3. NaCl-solution 0,9 $^0/_0$ or 1 *gramme molecule* CHI_3 *to* 1.900000 *L of the NaCl-solution.*

   Undoubtedly the effect will be visible in a still stronger dilution. (Compare Table IV).

3. This effect of an Iodoform-solution cannot be ascribed to ions of I, for these are found to impede phagocytosis. *We must think here of the property of Iodoform to dissolve in the fatty outer layer of phagocytes (the so-called lipoid membrane); hence the membrane is softened, the surface-tension diminishes and the motion*

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[1] ARLOING. Article: Chloroforme, in Richet's Dictionaire de Physiologie.

of the phagocytes is made easier. A more rapid taking up of carbon particles must be the consequence of this.

4. *If this interpretation is the correct one, then other substances, soluble in fat, must also be able to effect an accelerated phagocytosis.* This result was indeed arrived at for all substances of various composition experimented upon, viz. Chloroform, Chloral Benzene, Camphor and Turpentine.

5. *Chloroform* was seen to promote phagocytosis *even in a concentration of* 1 *to* 5.000000. In a concentration 1 vol. to 500.000 the increase of phagocytosis amounted to 43 $^0/_0$. In stronger solutions this value was smaller and the stronger the solution the more the accelerating effect diminished. This must be attributed to a second factor coming into play, viz. paralysis of the protoplasm-motion, which factor manifests itself but little in a very weak solution.

6. Benzene e. g. was found *to have the most favourable effect on phagocytosis in a dilution of* 1 *to* 100.000.

7. A saturated solution of *Camphor* in NaCl-solution of 0,9 $^0/_0$ caused a fairly considerable increase of phagocytosis. But if this saturated solution was diluted with 100 times its volume of NaCl-solution then the acceleration was again more considerable viz. 32 $^0/_0$.

8. *Turpentine* in a dilution of 1 : 100.000 effected an increase of phagocytosis of 24.7 $^0/_0$. but in a solution of 1 to 25.000 instead of an increase it caused a *decrease* and that of more than 80 $^0/_0$! With *Chloral* the results were exactly the same.

9. The facts mentioned in 1—8 deserve our attention from two points of view:

a. They correspond entirely with those observed by J. Loeb in the artificial fertilization of the eggs of the sea urchin (echinus) and the star fish. By allowing namely substances dissolving fat to act upon these eggs he could effect the development of these into larvae.

In our opinion the explanation of this fact must be sought in the circumstance that by the weakening of the lipoid egg-membrane the protoplasm-motion on which the division-process is based, is facilitated or rendered possible. This agrees with the observation of R. S. Lillie that the mere warming of the eggs may bring about the division, a fact which was confirmed by J. LOEB.

The analogy between the effect of substances dissolving fat on the development of eggs on the one hand, and on the acceleration of phagocytosis on the other, may be carried on still further, if we bear in mind that a copious action of these substances causes paralysis in the phagocytes (or destruction, as with camphor) and cytolysis in the eggs.

b. It is a well-known fact that narcotics stimulate when applied in small quantities and only paralyse in greater amounts. Viewed in the light of the facts we have observed about phagocytes, the explanation is easy to find.

At first, namely, the lipoid membrane of the cells is weakened, consequently the surface-tension grows less, and the rapidity of motion, the activity becomes greater. As soon as a greater amount of the narcotic has entered, its paralyzing effect on protoplasm becomes manifest.

For some general considerations see p. 998 and foll.

Groningen, January 1911.

Physiology. — *"On the stimulating effect of Chloride of Calcium and of intestinal mucous membrane extract on the action of Trypsin."* By MR. E. HEKMA. (Communicated by Prof. H. J. HAMBURGER).

(Communicated of the meeting of February 25, 1911).

The investigation reported on in the following pages found its starting-point in an investigation relating to the question whether chloride of calcium possesses the property of activating trypsinogen. Several investigators, particularly LARGUIER DES BANCELS [1]), DELEZENNE [2]), ZUNZ [3]) and recently also miss AYRTON [4]) have attributed to calcium

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[1]) LARGUIER DES BANCELS. C. R. Soc. de Biol. 1895, p. 130.

[2]) DELEZENNE. C. R. Soc. de Biol. 1905, p. 476, 523, 614; 1906, p. 1070; 1907, p. 274.

[3]) ZUNZ. Annal. de la Soc. Roy. des Sc. Méd. et Nat. de Bruxelles. XVI. 1907.

[4]) Miss B. AYRTON. Collected Papers. Inst. of Physiol. University College London. Vol. XV. Edited by E. H. STARLING.

salts, and also to some other salts, the faculty of rendering inactive pancreatic-juice, or pancreatic extract, active with respect to albumen, in other words, capable of activating trypsinogen.

During the last few months I too have made a number of experiments with a view to obtaining, if possible by an independent investigation, a confirmation of the results arrived at by these authors, whose conclusions are for the rest pretty well identical. I became aware that an investigation as to the activating effect of chloride of calcium on trypsinogen (I have not as yet extended my investigation to other salts) though apparently simple, was attended with considerable difficulties. Hence my experiments on the subject have not yet led to any definite result so far as *the activating effect* of chlorid of calcium on *trypsinogen* is concerned. But in the course of this investigation some other facts have come to light which seem to me to be worth publishing, the more so as the difficulties encountered, will be to some extent set forth and explained by them.

In the course of the above-mentioned investigation it was namely discovered that *chloride of calcium* has the property of materially stimulating the action of trypsin, when already active in itself and free from trypsinogen. The same fact was observed about intestinal mucous membrane extracts, but in a much slighter degree.

There is no need to point out that *activating* trypsinogen (i. e. transforming inactive trypsinogen into active trypsin) and stimulating the action of trypsin (i. e. stimulating into greater activity the ferment when free from trypsinogen and already active as it is) are two entirely different notions.

It has already been said that a further investigation relating to this stimulating action was begun on account of observations made in some experiments, which were carried out to study the activating effect of chloride of calcium on trypsinogen. We subjoin some of the experiments made. (Tables I and II). Beforehand it must be mentioned that the pancreatic-juice experimented with, was obtained by pressing out a pig's pancreas, likewise that the extracts from the intestinal mucous membrane were prepared by extracting the scraped-off intestinal mucous membrane, and filtrating it after some time. Further that in all the experiments discussed in this paper, we used for albumen: coagulated white of hens' eggs, according to METT's well tried method, and finally that wherever in this composition chloride of calcium is spoken of, the salt without water is meant.

From the experiment detailed in Table I we may draw the following conclusions:

TABLE I.

		Digestion of the egg-white-columns in m.m. after	
		24 hours	2 × 24 hours
1	Pancreatic juice: 3 drops + $2^0/_0$ NaFl-solution: 5 c.c.	8	18
2	" : 3 " + extract in $2^0/_0$ NaFl sol.: 5 c.c.	12	22
3	" : 3 " + boiled extract in $2^0/_0$ NaFl sol. 5 c.c.	9	19
4	" : 3 " + distilled water: 5 c.c.	8	12
5	" : 3 " + $0.4^0/_0$ $CaCl_2$ sol.: 2½ c.c. + water: 2½ c.c.	12	25
6	" : 3 " + $1^0/_0$ $CaCl_2$ sol.: 2½ c.c. + water: 2½ c.c.	12	26
7	" : 3 " + $1^0/_0$ $CaCl_2$ sol.: 2½ c.c. + $2^0/_0$ NaFl sol.: 2½ c.c.	6	8

In the first place it appears from 1) that the pancreatic-juice contained trypsin, for we observe that in a medium of a $2^0/_0$ sol.NaFl a not inconsiderable digestion had taken place. If the pancreatic-juice had been entirely free from trypsin, in other words if it had contained nothing but trypsinogen, then no digestion of albumen would have taken place in a medium of a $2^0/_0$ NaFl-solution. From a comparison between 1) and 2) it appears that in 2) the albumen-digestion is greater than in 1). It followed from this that probably not all trypsinogen had passed into trypsin, because it had to be assumed that in 2) trypsinogen had still been activated by the extract from the intestinal mucous membrane.

Since this pancreatic-juice contained already free trypsin, we evidently could draw no conclusions from it as to trypsinogen being *activated* by chlorid of calcium; from this point of view, therefore, this experiment had to be looked upon as having failed.

On comparing 4) with 1) we see that after after 48 hours the digestion in 4) is considerably less than in 1). This result must be attributed to the fact that in 1) the bacteria-development was impeded by the NaFl-solution, whereas in 4) the bacteria were able to develop themselves freely.

Bacteria (at least some bacteria, I shall, however, not enter into this subject, as it does not bear on the matter under consideration) have directly opposite effects on trypsin and on trypsinogen, as I gathered from a great many experiments. Whilst on the one hand *trypsinogen* can be *activated* [1]) by the action of bacteria, on the other hand the action of *trypsin* is greatly *impeded* by bacteria (or perhaps by the decomposition-products of albumen at the joint action of trypsin and bacteria. The pancreatic-juice experimented upon containing comparatively little trypsinogen and much trypsin, the antitryptic action of the bacteria prevailed in this case upon its activating influence, which also appears from the fact that in 4) and 1) the albumen-digestion is still the same after 24 hours, whilst after 48 hours (when all the trypsinogen in 4) could be expected to have passed into trypsin) it is considerably less in 4) than in 1).

Obviously this experiment gives support to the opinion that the influence of micro-organisms, in experiments relating to the activation of trypsinogen (and I may add by the way: likewise in experiments on antitryptic factors) should by no means be disregarded.

The condition that the action of bacteria must be effectually obviated in such experiments, e.g. when studying the effect of calcium-salts on the activation of trypsinogen, forms one of the difficulties I alluded to just now. The more so, as it stands to reason that in experiments with Ca-salts no NaFl may be used, which we can also gather for instance from 7) Table I. As we see the digestion in 7) is very inconsiderable. This must be attributed to the Fl. of the NaFl having formed in this case insoluble $CaFl_2$ with the Ca of $CaCl_2$. The precipitate $CaFl_2$ had sunk to the bottom of the test-bottle, carrying part of the albumen of the pancreatic juice with it. Hence the Mett-tubes had got enclosed in a thick precipitate of $CaFl_2$ and pancreatic albumen, in consequence of which the trypsin-action on the Mett's albumen-columns could of course not assert itself so well.

Finally on comparing in Table I the numbers 5) and 6) with 1) and 2), we might at first sight be inclined to assume that under the influence of $CaCl_2$ trypsinogen had been activated, the digestion in 5) and 6) being considerably greater than in 1), and as great, nay even somewhat greater than in 2). On second thoughts I arrived at the conclusion that in this case not merely the *activating* effect of $CaCl_2$ had to be considered, that at any rate there must also be other reasons for the greater digestion in 5) and 6). Indeed it appears from 2) that in this case the amount of trypsinogen could only be

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[1]) For further particulars on this subject see an article of mine in the Archiv. für Anat. und Physiologie 1904 p. 343.

small, whilst as regards trypsin, the antitryptic effect of the bacteria would have manifested itself in 5) and 6) as strongly as in 4), if not another factor had been present, which promoted in 5) and 6) the trypsin-action more than it was counteracted by the bacteria.

These considerations suggested the idea to me that chlorid of calcium might perhaps have the property of stimulating the activity of trypsin.

This would, moreover, explain the results of these, and such like experiments, for I repeatedly found similar results.

As a type of the experiments, in which the pancreatic juice used, was free from trypsin, containing nothing but trypsinogen, we may quote the following (Table II).

TABLE II.

	Amount of Pancreatic-juice used	Fluids added	Digestion of two albumen-columns in m.m. after: 24 hrs.	2×24 hrs.
1)	2 drops	+ 2% NaFl-solution: 10 c.c.	0	0
2)	2 "	+ intestinal mucous membrane extract in 2% NaFl-solution: 10 c.c.	5.4	9
3)	2 "	+ boiled intestinal mucous membrane extract in 2% NaFl-solution: 10 c.c.	0	0
4)	2 "	+ 1% chlorid of calcium-solution: 5 c.c. + 2% NaFl-solution: 5 c.c.	0	0
5)	2 "	+ 1% chlorid of calcium-solution: 5 c.c. + water: 5 c.c.	2	6
6)	2 "	+ water: 10 c.c.	1.6	4

In the first place it appears from 1) and 3) of this experiment (Table II) that in this case the pancreatic-juice used, contained only trypsinogen and no trypsin. Regarded therefore as an investigation concerning the activating effect of chlorid of calcium on trypsinogen, the experiment could not be seriously found fault with. Except that in this experiment no sterile water and sterile $CaCl_2$-solution had been used, which evidently should have been done in experiments on the activating effect of $CaCl_2$ on trypsinogen. I intentionally quote an experiment in which no sterile water and no sterile $CaCl_2$ were used, as being more to the purpose. An experiment like the one, detailed in Table II may even more strongly than the preceding one (Table I) create an impression, when we compare 5) and 6), that trypsin might be activated by chlorid of calcium. In 6) the activation has undoubtedly been effected by the bacteria, which have developed themselves in the non-sterile water (+ pancreatic-juice); in 5) the greater activation might have been caused by the joint action of bacteria and $CaCl_2$. And since in 5) the digestion was greater than in 6) there were plausible reasons for concluding that chlorid of calcium had contributed to the activation of trypsinogen. Still, as my attention had been directed to the possibility of a stimulating action of chlorid of calcium on trypsin, the difference in digestion between 5) and 6), when looked at from this point of view, might find an explanation in this sense. Further discussion of this experiment may be esteemed superfluous; I thought it advisable to insert it here as an additional proof that we have to be very careful about conclusions as to a contingent activating effect of chlorid of calcium on trypsinogen.

Whilst on the ground of the preceding observations it seemed not unlikely that chlorid of calcium might have a stimulating effect on trypsin itself, a closer investigation was begun now in order to test this supposition by means of experiments. For this purpose I made use of some commercial trypsin-preparations, viz. that of GRÜBLER and that of MERCK. As the activity of the preparations in the laboratory was found to be very slight with regard to coagulated albumen I ordered fresh preparations a few times. I informed the firm of GRÜBLER as to this slight activity, upon which this firm sent me, as I was informed, a newly-made preparation.

Yet the activity of this preparation was no greater than that of the preceding ones. That is to say as regards albumen, as regards fibrin the action of these preparations left nothing to be desired. By making the concentrations of the trypsin-solutions (suspensions) considerably stronger than prescribed by the firm I could use these commercial preparations for my purpose. The trypsin-solutions (suspensions) were prepared by means of soda-solutions. As the use of Na_2CO_3 seemed liable to some objections, however, owing to the slight solubility of the $CaCO_3$, resulting from $CaCl_2$ being added, I made use of very weak (as a rule 0.1 $^0/_0$) solutions of Na_2CO_3.

That there was no objection to the use of a 0.1 $^0/_0$ sol. of Na_2CO_3 is seen from the following experiment, which for the rest served to investigate the stimulating effect of $CaCl_2$ on trypsin-action (Table III).

For this experiment 1 gramme of trypsin-GRÜBLER was dissolved in 100 cc. Na_2Co_3 of 0.1 %. The trypsin dissolved in it with a slight opalescence, the solution was not filtrated before it was used. To 5 cc. of this solution were added 5 cc. water and 5 cc. $CaCl_2$-solution, respectively.

TABLE III.

	Digestion of two albumencolumns in m.m. after:	
	2×24 hrs.	3×24 hrs.
1) Trypsin sol. 1/100: 5 c.c. + water: 5 c.c.	3	4
2) Trypsin sol. 1/100: 5 c.c. + $CaCl_2$ sol. of 1%: 5 c.c.	9	15
3) Trypsin sol. 1/100: 5 c.c. + $CaCl_2$ sol. of 1%: 2½ c.c. + water: 2½ c.c.	10	15

From this experiment it appears that in 2) and 3) where $CaCl_2$-solutions had been added to the trypsin-solutions, the albumen digestion was considerably greater than in 1), where water had been added. We observe that the trypsin itself (1) showed very little activity as regards coagulated albumen, though as I observed before, 1 gramme of trypsin had been taken upon 100 c.c. Na_2Co_3 of 0.1 % (an addition of an equal volume of water making the concentration 1/200). And further that this power was considerably heightened under the influences of a 1 % and a 0.5 % $CaCl_2$-solution, respectively.

Still from this result it might not be concluded yet that $CaCl_2$ had promoted the action of trypsin. And that, for this reason: the trypsin-preparations might still contain some trypsinogen, which might have been turned into trypsin by $CaCl_2$.

Before continuing our experiments in this direction, we therefore had to settle first whether the trypsin-preparation used, was indeed free from trypsinogen. This question could be solved by adding in a following experiment also intestinal mucous membrane extract to the trypsin-solution and at the same time the boiled extract. [It is generally held, and in my opinion absolutely certain (Cf. 3) Table II) that boiling renders inactive the substance in the intestinal mucous membrane extract which causes trypsinogen-activation].

In order to solve the question whether the trypsin was free from trypsinogen or not, it seemed advisable to make a double experiment by using in the first place a solution of trypsin in 0.1 % Na_2CO_3-sol. (Table IV A 1—6) and secondly a solution of trypsin in a 2 % Na Fl-solution (Table IV B 1—6).

As was observed already the trypsin-GRÜBLER used for this experiment (Table IV) was the same as that applied in the preceding one (Table III); instead of a trypsin-concentration 1/100, 1/50 was used. Moreover, as appears from this Table, an intestinal mucous membrane extract in water as well as in 2 % NaFl-sol. was taken. It ought to be mentioned that the proper trypsinogen-activating effect of the extracts of the intestinal mucous membrane was in all cases tested by means of pancreatic-juice.

TABLE IV.

A	Trypsin-GRÜBLER 1 gramme to 50 c c. Na_2CO_3 sol. of 0.1 %	Fluids added	Digestion of the two albumen columns in m.m., after:		
			24 hrs	48 hrs	72 hrs
1)	3 c.c.	water: 2 c.c.	2	4	5
2)	3 c c.	$CaCl_2$ sol. (1 %): 2 c.c.	8	16	20
3)	3 c.c.	intest. mucous membrane-extract in 2 % NaFl-sol. 2 c.c.	4	8	12
4)	3 c.c.	intest. muc. membr.-extr in water: 2 c.c.	3.60	7	10
5)	3 c.c.	Boiled int. mucous membrane-extract in 2 % NaFl-sol.: 2 c.c.	4	8.50	13
6)	3 c.c.	Boiled int. mucous membrane extract in water: 2 c.c.	8	8	11
B	Trypsin-GRÜBLER 1 gramme to 50 c c. of a 2 % NaFl-sol.				
1)	3 c.c.	Water: 2 c.c.	3	6	8
2)	3 c.c.	$CaCl_2$-sol. (1 %): 2 c.c.	0	0	0
3)	3 c.c.	intest. mucous membrane-extract in 2 % NaFl-sol. 2 c.c.	4	8	12
4)	3 c.c.	intest. muc. membr.-extr. in water: 2c.c.	4.40	8.50	12
5)	3 c.c.	Boiled int. mucous membrane-extract in 2 % NaFl sol.: 2 c c.	4	9	13
6)	3 c.c.	Boiled int. mucous membrane-extract in water: 2 c.c.	4	8 50	12

From the preceding experiment (Table IV A and B) we may conclude what follows. Comparison between A 3—6 and A, and likewise between B 3—6 and B teaches that also in this experiment the intestinal mucous membrane extracts have had a favourable effect on the trypsin-action. From the result that the albumen-digestion in A 3, 4, 5, and 6, and likewise in B 3, 4, 5, and 6 differed little or nothing, that consequently the *boiled* extracts of the intestinal mucous membrane were found to have the same favourable effect as the unboiled ones, we may conclude that in the trypsin-preparation used, no *trypsinogen* was present. The fact that in spite of this the albumen-digestion in A 3—6 was found to be considerably greater than in A_1, whilst this was also the case with B 3—6 and B_1 respectively, could in my opinion be explained only by assuming *that in the extracts of the intestinal mucous membrane, in other words, in the intestinal mucous membrane, a substance is found which can promote the trypsin-action, a substance which (contrary to the substance activating trypsinogen) could not be rendered inactive by being boiled.*

From the result that the trypsin used, was found to contain no trypsinogen, it also follows that the favourable effect of chlorid of calcium, observed in the preceding experiment (Table III) must be attributed to *the heightened action of trypsin, occasioned by chlorid of calcium.* The intensifying action of chlorid of calcium, as regards trypsin, likewise manifests itself, and that very obviously, in the last experiment (Table IV A and B). For in A_2 the albumen digestion is seen to be much greater than in A_1. That in B_2 no digestion took place at all, must undoubtedly be attributed to a precipitate of $CaFl_2$ being formed here, which had sunk to the bottom of the test-bottle, and surrounded the Mett's tubes, so that the trypsin-action could not manifest itself. Comparison between A 3—6 and A_2 shows, moreover, that the stimulating effect of the intestinal mucous membrane extract is a slighter one than that caused by chlorid of calcium, at least in the concentration used[1].

Further it may be concluded from A 3 and 5 and B 3 and 5 (Table IV) that *the substance deriving its origin from the intestinal mucous membrane, and promoting the trypsin-action, is in all probability no calcium-salt.* For it may be assumed that a calcium-salt, if it were present in the extracts used, would have been precipitated by NaFl as insoluble $CaFl_2$. This last observation likewise holds good,

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[1] An investigation as to the influence of the concentration of the chlorid of calcium-solution, and also as to the effect of some other soluble calcium-salts on trypsin, is in progess, but has not yet been completed.

of course, for other salts which may be found in extracts of the intestinal mucous membrane, in other words in the intestinal mucous membrane itself, so far as they form insoluble compounds with NaFl.

The results described in connection with the tables inserted, were confirmed by other experiments made with the same view, which, as was observed already, were carried out with different trypsin-preparations of Grübler and of Merck. We subjoin one more experiment, made with trypsin-Merck. (Table V).

TABLE V.

Trypsin-Merck 1 gramme to 50 c.c. Na_2CO_3-sol. of 0.1 $^0/_0$	Fluids added	Digestion of the two albumen-columns in m.m. after		
		24 hrs	48 hrs	72 hrs
3 c.c.	Water: 2 c.c.	4	10	11
3 c.c.	$CaCl_2$-sol. of $1^0/_0$: 2 c.c.	8	20	empty
3 c.c.	Int. muc. membr. extr. in $2^0/_0$ NaFl: 2c.c.	4.40	16	empty
3 c.c.	Int. muc. membr. extr. in water: 2 c.c.	5.50	15	empty
3 c.c.	Boiled int. muc. membr. extr. in $2^0/_0$ NaFl: 2 c.c.	5.60	15	empty
3 c.c.	Boiled int. muc. membr. extr. in water: 2 c.c.	6	16	empty

It is seen that the result of this experiment (Table V) is analogous to that of the preceding one. Further remarks are not suggested by Table V, except that comparison with Table IV, shows that the trypsin-Merck was somewhat more active than the trypsin-Grübler, a fact which could invariably be established in the experiments.

SUMMARY.

1. The experiments described above have shown that chlorid of calcium can increase to a considerable extent the activity of trypsin which contains no trypsinogen.

2. This promotive effect of chlorid of calcium on trypsin should not be confounded with the activating effect of chlorid of calcium on trypsinogen, which latter property is ascribed to this salt by several authors.

3. The extracts of the intestinal mucous membrane were also found to possess the property of being able to increase the action of trypsin, to a smaller extent, however, than chlorid of calcium.

4. The substance originating in the intestinal mucous membrane, which brings about this action, is not destroyed by being boiled, and is in all probability no calcium.

5. Besides a substance which, as we know, possesses the faculty of being able to activate trypsinogen, which substance is rendered inactive by being boiled, the intestinal mucous membrane contains, therefore, also another substance which has the power of stimulating active trypsin, a substance which is not rendered inactive by being boiled.

Groningen, January 22nd 1911. *Physiological Laboratory.*

Physics. — "*Isotherms of monatomic substances and of their binary mixtures. IX. The behaviour of argon with regard to the law of corresponding states.*" By Prof. H. KAMERLINGH ONNES and C. A. CROMMELIN. Comm. N°. 120*a* from the Physical Laboratory at Leiden.

(Communicated in the meeting of February 25, 1911).

§ 1. *The mean reduced surface of state for monatomic substances.* A difficulty which is by no means small is introduced into theoretical investigations dealing with the equation of state by the fact that, for every substance, and, in particular, for substances of simple molecular construction, the region that has been experimentally investigated extends over a small range of reduced pressure and of reduced temperature. If the law of corresponding states were strictly obeyed, this difficulty could be obviated by reducing and then combining with each other the regions investigated for the various substances. In this way the mean reduced equation of state has been synthesized: in the form VII. 1 [1]). It has been obtained from AMAGAT's observations on hydrogen, oxygen, and nitrogen, YOUNG's on isopentane and AMAGAT's and RAMSAY and YOUNG's on ether. In this way the equation of state has been obtained for an imaginary substance which, if further amplified by the disturbance function [2]) for the neighbourhood of the critical point, is suitable for all calculations in which the validity of the law of corresponding states is assumed. And this equation is of particular use in tracing deviations from the law of corresponding states, for it affords a suitable means of easily comparing

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[1]) Suppl. N°. 19 (May 1908).

[2]) Proc. Febr. 1908. Comm. N°. 104.

individual results, which cannot be satisfactorily represented by a special equation of state, with results obtained for other substances, and, particularly, with results obtained for those substances which have served for the calculation of equation VII. 1. When deviations of some particular substance from the imaginary substance in the same reduced state have been calculated, then, the far more concise deviations from VII. 1. may replace the actual results of the experiments themselves.Such deviations were determined for each of the substances used in the synthesis of equation VII. 1. with respect to whose reduced surfaces of state that of VII. 1. plays the part of a quasi-enveloping surface. The critical temperatures of the substances can greatly influence the differences existing between the separate surfaces; the peculiarities of the molecules, however, can influence them, too, in another way.

The object we had in view in our research upon the isotherms of monatomic substances was to obtain, in the same manner as that in which equation VII. 1. was obtained, a mean reduced equation of state in the synthesis of which observations on monatomic substances should exclusively be used. Unless in the structure of the various atoms of the monatomic substances further peculiarities are discovered which influence the equation of state, then, the only influence exerted upon the form of the reduced surface is that of the critical temperature. This influence will manifest itself in the deviations of the special equations from the mean equation undisturbed by other possible factors. And it is to be expected that the special surfaces of state for the various monatomic substances should systematically differ from the enveloping surface and from each other in such a manner that a gradual transformation would change the xenon [1]) surface into those for krypton, argon, and neon, to finally assume a limiting shape in the case of helium [2]). From the sequel, in which is given a first, but very small, step in the desired direction, it is evident that the mean reduced equation of state for monatomic substances which we desire to obtain, and which we shall indicate by $VII_{mon.}$, will exhibit important characteristic differences from the general mean equation VII. 1.

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[1]) We shall, for the present, leave out of consideration substances of higher critical temperature.

[2]) It was remarked in 1881 that a separate equation of state would have to be applied to each group of substances having similar molecules. (H. KAMERLINGH ONNES. Verh. Kon. Akad. 1881, Arch. neérl. 30, p. 101). The group of monatomic substances has been made a subject of special study from this point of view by H. HAPPEL, see Ann. d. Phys. (4). 13. 340. 1904.

§ 2. *Comparison of argon isotherms*[1]) *with those of isopentane* (YOUNG)[2]), *ether* (RAMSAY *and* YOUNG)[3]) *and carbon dioxide* (AMAGAT)[4]) *between the reduced temperatures* 1.0000 *and* 1.1323.

In order to obtain a systematic comparison from the point of view of the law of corresponding states between the results obtained for argon and those for other substances, we have in the manner indicated in § 1, calculated the differences between the observed data for the various substances and the values obtained from VII. 1[5]). To begin with, the critical temperature and pressure already published[6]) were used in the calculation of the virial coefficients for argon according to VII. 1, and, from these coefficients, deviations from VII. 1 were obtained. It appeared to be most suitable to work with percentage deviations of pv from values of pv given by equation VII. 1[7]).

The virial coefficients are given in table I and the differences in table II.

The deviations for isopentane, ether and carbon dioxide from VII. 1. were calculated a considerable time ago; they form part of an extensive research upon the differences between the empirical equations of state for these substances as expressed by their deviations from the general mean reduced equation, of which only a very small part has yet been published. From amongst these, deviations are taken which can be compared with the argon isotherms between —100° C. and the critical point, that is, those which lie in the same region of reduced temperature as the argon isotherms. The deviations for all four substances were then united in one diagram in which the deviations were plotted as functions of $log\ \lambda\mathfrak{v}$ in which $\lambda = \frac{p_k v_k}{T_k}$ and $\mathfrak{v} = \frac{v}{v_k}$.

Hence, the critical volume does not appear in the expression

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[1]) Proc. Dec. 1910, Comm. No. 118*b* and C. A. CROMMELIN. Thesis for the doctorate, Leiden, 1910.

[2]) S. YOUNG, Proc. phys. soc. London, 1894/95, p. 602.

[3]) W. RAMSAY and S. YOUNG Phil. Trans. 178. 57. 1887.

[4]) E. H. AMAGAT, Ann. de chim. e. d. phys. (6) 29, June and Aug. 1893.

[5]) For a critical examination of the observations it is also very desirable to substitute deviations from VII. 1. for the actual observations so as to eliminate experimental error, and to reduce to one common substance the results obtained by different observers. Our results for argon were treated in this fashion before being placed upon the diagram.

[6]) Proc. May 1910, Comm. N⁰. 115.

[7]) For the method by which these calculations are made, c.f. Proc. June 1901, comm. No. 71.

TABLE I.

Virial coëfficients for argon according to VII. 1.

t	$B_A . 10^3$	$C_A . 10^6$	$D_A . 10^{12}$	$E_A . 10^{18}$	$F_A . 10^{24}$
+ 20°.39C.	− 0.61763	+ 2.21916	+ 4.32836	+ 7.6045	− 4.35430
0.00C.	− 0.77633	+ 2.21208	− 3.09635	+ 8.7321	− 4.98937
− 57.72C.	− 1.30816	+ 2.40867	− 0.67139	+ 10.5255	− 5.02409
87.05C.	− 1.66571	+ 2.73556	− 2.83014	+ 10.5566	− 3.93044
− 102.51C.	− 1.89979	+ 3.04873	− 4.10121	+ 10.4013	− 3.10842
− 109.88C.	− 2.02794	+ 3.25078	− 4.76310	+ 10.3251	− 2.69045
− 113.80C.	− 2.10156	+ 3.37635	− 5.15599	+ 10.2947	− 2.47655
− 115.86C.	− 2.14198	+ 3.44818	− 5.35020	+ 10.2837	− 2.35600
− 116.62C.	− 2.15723	+ 3.47581	− 5.41531	+ 10.2806	− 2.31432
− 119.20C.	− 2.21026	+ 3.57411	5.67996	+ 10.2759	− 2.17669
− 120.24C.	− 2.23230	+ 3.61597	− 5.78950	+ 10.2764	− 2.12239
− 121.21C.	− 2.25318	+ 3.65616	− 5.89340	+ 10.2783	− 2.07246
− 130.38C.	− 2.46836	+ 4.10021	− 6.96374	+ 10.3966	− 1.66293
− 139.62C.	− 2.72584	+ 4.69951	− 8.27734	+ 10.8045	− 1.42979
− 149.60C.	− 3.06753	+ 5.59572	− 10.45136	+ 11.8440	− 1.53961

$\lambda v = \frac{p_k}{T_k} v$; only the critical temperature and pressure are used in the calculation of λv, while, when different substances are being compared with each other a single but undetermined value is ascribed to λ for all substances. This method which has already been adopted on former occasions [1] has the great advantage that it is not necessary to use the critical magnitude which is most uncertain, viz. the critical volume, and only well defined magnitudes are employed. To make λ the same for all substances, although it varies distinctly for the various substances [2], may well appear somewhat strange at first sight. The systematic deviations of the various equations from VII. 1 revealed in the different values of λ are not, however, the only systematic deviations to which expression will here be given. There

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[1] Proc. June 1901, Comm. N°. 71.

[2] Proc. Febr. 1907, Suppl. N°. 14.

TABLE II.

Percentage deviations of pv_{Λ} from $pv_{\Lambda}(C)$ of the general mean reduced equation VII. 1.

d_{Λ}	$O-C$ in %	d_{Λ}	$O-C$ in %	d_{Λ}	$O-C$ in %	d_{Λ}	$O-C$ in %	d_{Λ}	$O-C$ in %	d_{Λ}	$O-C$ in %
+ 20°.39 C.		0°.00 C.		— 57°.72 C.		— 87°.05 C.		— 102°.51 C.		— 109°.88 C.	
20.499	0.0	20.877	0.0	23.509	+0.1	25.152	+0.3	25.571	+0.5	26.242	+0.6
25.759	0.0	26.581	—0.1	[28.575	—0.2]	34.467	+0.1	35.077	+0.4	34.807	+0.8
32.590	0.0	32.302	—0.1	33.793	—0.2	55.822	—0.1	[47.893	+0.9]	65.142	+0.8
35.759	0.0	37.782	—0.2	48.116	—0.3	71.444	—0.2	[53.752	+0.9]	87.176	+0.8
47.319	0.0	51.840	—0.5	64.948	—0.4	94.625	—0.7	62.240	+0.4	102.76	+0.5
59.250	—0.1	65.325	—0.7	90.695	—0.9	119.84	—1.0	[69.954	+0.9]	125.56	+0.2
								84.002	+0.2	148.32	—0.2
								95.802	0.0	180.84	—1.0
								115.88	—0.4		
								135.65	—0.7		
								158.01	—1.2		
— 113°.80 C.		— 115°.86 C.		— 116°.62 C.		— 119°.29 C.		— 120°.24 C.		— 121°.21 C.	
67.078	+1.0	69.947	+1.1	26.480	+0.9	26.871	+1.0	72.627	+1.7	27.326	+1.1
88.889	+1.0	91.308	+1.2	34.939	+0.8	34.965	+1.2	82.816	+2.0	35.283	+1.3
106.68	+0.7	108.02	+0.9	68.630	+1.2	70.314	+1.4	99.246	+2.0	71.459	+1.8
129.17	+0.5	131.51	+0.6	90.563	+1.2	70.481	+1.0	118.51	+1.8	85.580	+2.0
152.71	0.0	155.12	+0.1	110.19	+0.9	83.257	+1.1	136.31	+1.7	100.33	+1.8
155.40	0.0	179.94	—0.5	133.69	+0.7	96.834	+1.5	165.79	+0.9	[123.85	+1.9]
182.13	—0.5	[183.35	+1.8]	159.71	+0.2	98.863	+1.0	206.57	+0.1	148.95	+1.6
184.82	—0.7	235.47	—1.7	161.75	0.0	124.97	+0.6	280.25	—0.7	170.05	+0.9
212.99	—1.1	319.52	—2.9	[186.15	—0.4]	[143.71	+0.9]	338.95	—0.5	234.13	—0.2
				210.02	—0.9	156.36	—0.1			333.75	—0.1
				[260.61	—2.0]	[172.25	+0.6]				
				331.29	—2.8	222.69	—1.8				
						275.02	—2.8				
						336.89	—3.4				
— 130°.38 C.		— 139°.62 C.		— 149°.69 C.							
27.394	+1.7	28.422	+2.4	29.183	+3.8						
31.583	+1.2	35.573	+2.9	34.646	+4.4						
34.726	+2.0										
55.807	+2.9										
65.125	+3.2										
77.821	+4.2										
101.71	+3.3										

is, therefore, no danger in uniting this one kind of deviation with the other ones in the common representation which we try to obtain for them. According to the method we followed it appears to be possible to unite all deviations from the law of corresponding states in a single representation as definite as can be desired for the present; but, of course, we do not mean to say that it might not be found more suitable in a more extended and more searching study of the deviations from the law of corresponding states to adopt a different method of summarising these deviations.

In order to be able to ascribe the same value to λ in every case, all the volumes must be expressed in the same unit. This was not the case with the observations which are now being dealt with, so that some reductions were found necessary. v_A, volumes in the argon isotherms and in the carbon dioxide isotherms are expressed in terms of the experimental normal volume, while those in the isopentane and ether isotherms are expressed in terms of the number of cubic centimetres per gram of the substance. Since we wished to express λv in terms of the theoretical normal volume for all the substances we calculated its values according to the following expressions:

for argon and carbon dioxide: $\lambda v = \frac{p_k}{T_k A_{A_0}} v_A$;

for isopentane and ether: $\lambda v = \frac{p_k \gamma}{T_k A} v_A$ [1]

In these expressions $A_{A_0} = \frac{1}{v_N}$ is the ratio of the experimental to the theoretical normal volume, and γ is the specific mass [2]) in grams per c.c. at normal temperature and pressure.

Values of *log* λv, were marked off as abscissae, and as ordinates values of the common logarithms of the reduced temperatures. Lines parallel to the *log* λv axis represent the course of the equation VII. 1, while deviations are marked off from these lines, (positive above, negative below) in such a way that a $1^0/_0$ deviation corresponds to 5 mm. on the accompanying diagram. We shall call this method of exhibiting the deviations in a diagram "arranging according to *log* t the deviations expressed as functions of *log* λv." From this drawing which, since it contains the deviations for the various substances at the different reduced temperatures (the observation temperatures of the isotherms), has been somewhat abridged, the deviations for each

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1) Arch. neérl. (2) 6, 874. 1901, Comm. No. 74.

2) In all these considerations we may neglect the difference between the specific mass and the density (number of grams pro m. L.).

substance for successive values of $log\ \lambda v$ were now read off, and the values thus obtained were then graphed as functions of $log\ t$, arranged according to $log\ \lambda v$. By reading from the graphs thus deduced, the deviations for the various substances were brought to the same reduced temperature. For these reduced temperatures were chosen the temperatures of the argon isotherms, viz.

1.00816, for argon corresponding to —121°.21 C.
1.01460, ,, ,, ,, ,, —120°.24
1.02151, ,, ,, ,, ,, —119°.20
1.03863, ,, ,, ,, ,, —116°.62
1.04368, ,, ,, ,, ,, —115°.86
1.05735, ,, ,, ,, ,, —113°.80
1.08337, ,, ,, ,, ,, —109°.88
1.13229, ,, ,, ,, ,, —102°.51

And finally, the deviations were graphed as functions of $log\ \lambda v$, and all reduced to the same temperatures. This diagram is reproduced on the Plate accompanying this Communication. The deviation curves for the reduced temperatures 1.01460 and 1.04368 could not be drawn on it, as in order to do this distinctly the scale would have to be made too great. The rectangle on the right hand lower portion of the diagram borders the immediate neighbourhood of the critical state. It is best, while employing this method of critically examining the deviations, to leave this region out of account provisionally, as otherwise one would have to allow for the influence of the disturbance function [1]. A description of the information afforded by this plate concerning the deviations of the various substances seems to us unnecessary; it speaks for itself, and gives clear expression to the systematic deviations of argon from the other substances in this region.

§ 3. *Calculation of certain data which are of importance in the discussion of deviations from the law of corresponding states.*

To get an idea of deviations from the law of corresponding states, certain data are usually calculated, and we are now able to obtain their values for argon from our former experiments. [2]

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[1] Proc. Febr. 1908. Comm. No. 104.

[2] Proc. May 1910, Comm. No. 115; Proc. Dec. 1910, Comm. No. 118*a*; Proc. Dec. 1910, Comm. No. 118*b*.

a. By substituting values of argon vapour pressures in the well known VAN DER WAALS vapour pressure equation[1])

$$\log \frac{p}{p_k} = f' \frac{T - T_k}{T}$$

and using common logarithms we get the following values for f':

t	p in atm.	f
−140°.80 C.	22.185	2.415
−134°.72C.	29.264	2.421
−129°.83C.	35.846	2.457
−125°.49C.	42.457	2.577

A cursory comparison of these values of f' with those for other substances shows us that the value for argon is closer to the theoretical value of f' at the critical point deduced from VAN DER WAALS's equation (1.737) than the values belonging to by far the greater number of other substances; this is what one would expect for monatomic substances. For carbon dioxide between −63° C. and the critical point f' goes from 2.84 to 2.97[2]); for isopentane[3]) between 130° C. and the critical point f' assumes a value between 2.75 and 2.95, while it further appears from the list published by KUENEN[4]) that, with the exception of monatomic substances and a few others such as hydrogen, oxygen, and carbon monoxide, values of f' are always still greater.

b. From the critical data already published, and from the weight in grams of one litre of argon at normal temperature and pressure which, according to RAMSAY and TRAVERS[5]) is 1.782, we found for the critical virial quotient

$$K_4 = \frac{RT_k}{p_k v_k} = 3.283.$$

This value is also closer to the theoretical value deduced from VAN DER WAALS's equation, 2.67, than those of almost all other

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[1]) J. D. VAN DER WAALS, Cont. I, p. 158.

[2]) J. P. KUENEN, Die Zustandsgleichung, p. 101, supplemented by KEESOM's measurements, Proc. Jan. 1904, Comm. N°. 88.

[3]) S. YOUNG l. c.

[4]) J. P. KUENEN, l. c. p. 142.

[5]) W. RAMSAY and M. W. TRAVERS, Proc. R. S. 67. 329. 1900.

substances, as is evident from the table of values given by KUENEN[1]) Hence, D. BERTHELOT's[2]) estimate is probably much too low.

c. Let us write the equation of the rectilinear diameter of CAILLETET and MATHIAS[3]) in the form

$$\frac{\varrho_{\text{liq}} + \varrho_{\text{vap}}}{2} = \varrho_{\text{k}} - a\,(T_{\text{k}} - T)$$

in which ϱ_{liq}, ϱ_{vap} and ϱ_{k} are the liquid, vapour and critical densities respectively and a is the slope of the diameter; calling

$$a_{\text{M}} = -a\,\frac{T_{\text{k}}}{\varrho_{\text{k}}}$$

the reduced slope, we can, with the liquid densities published by BALY and DONNAN[4]), and the value of the critical density already published, deduce from the isotherms

$$a = -0.003050$$
$$a_{\text{M}} = 0.9027.$$

The inclination of the diameter for argon is, therefore, unusually great — greater than has ever yet been found for any other substance, since a for most substances lies between -0.0005 and -0.0023[5]).

In connection with the foregoing, it is of interest to note that YOUNG[6]) discovered an intimate relationship for substances of higher critical temperature between the diameter's inclination and curvature and the values of the critical volume deduced from the law of the diameter. Representing the curved diameter by

$$\mathfrak{D} = \mathfrak{a}_{\text{d}} + \mathfrak{b}_{\text{d}}\mathfrak{t} + \mathfrak{c}_{\text{d}}\mathfrak{t}^2$$

in which

$$\mathfrak{D} = \frac{1}{2}\left(\frac{1}{\mathfrak{v}_{\text{liq}}} + \frac{1}{\mathfrak{v}_{\text{vap}}}\right).$$

then we obtain the following corresponding relations

$$-\mathfrak{b}_{\text{d}} < 0.93 \quad K_{4\text{d}} < 3.77 \quad \mathfrak{c}_{\text{d}} > 0$$
$$-\mathfrak{b}_{\text{d}} = 0.93 \quad K_{4\text{d}} = 3.77 \quad \mathfrak{c}_{\text{d}} = 0$$
$$-\mathfrak{b}_{\text{d}} > 0.93 \quad K_{4\text{d}} > 3.77 \quad \mathfrak{c}_{\text{d}} < 0.$$

On a former occasion[7]) the diameter was considered to be straight

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[1]) J. P. KUENEN, Die Zustandsgleichung, p. 60.

[2]) D. BERTHELOT, Journ. de phys. (3). 10. 611. 1901.

[3]) L. CAILLETET and E. MATHIAS, Journ. d. phys. (2). 5. 549. 1886.

[4]) E. C. C. BALY and F. G. DONNAN, Journ. chem. Soc. 81. 911. 1902.

[5]) E. MATHIAS, Le point critique des corps purs, p. 9 and 10.

[6]) S. YOUNG, Phil. Mag. (5). 50. 291. 1900.

[7]) Proc. Dec. 1910. Comm. N⁰. 118*a*.

for argon, and the assumption was then justified; we must, therefore put $\mathfrak{c}_d = 0$. But we have just found a value for K_4, and, since $K_4 = K_{4d}$[1]) it follows that

$$K_{4d} = 3.283 \text{ and } -\mathfrak{b}_d = a_M = 0.9027.$$

From this we may conclude either that argon is an exception to YOUNG's rule, or, as is not impossible, that its diameter is somewhat curved, in which case it would belong to the first group given by YOUNG. An accurate experimental research upon the diameter for argon would probably lead to important results bearing not only upon this point, but also upon the question of the value of the critical density of argon.

For oxygen MATHIAS and KAMERLINGH ONNES[2]) found

$$-\mathfrak{b}_d = 0.813\,, \quad K_{4d} = 3.346\,, \quad \mathfrak{c}_d = 0\,.$$

It appears, therefore, as if values of K_{4d} in YOUNG's criterion become smaller and smaller the lower the critical temperature of the substance.

d. We can, in the meantime, say nothing definite about the function

$$\left(T\frac{\partial p}{\partial T} - p\right)v^2$$

investigated by REINGANUM[3]) and by VOGEL[4]). An investigation of this point is, however, in progress.

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[1]) The subscript *d* in K_{4d} is used to indicate the fact that the value of the critical volume with which this number is calculated has been obtained from the diameter. Although the value here given for the critical virial quotient has been obtained from a value of v_k calculated from the isotherms, we have, nevertheless, assumed that we may write $K_4 = K_{4d}$, seeing that probably the two values of v_k obtained by the two different methods differ but little from each other. (See Comm. No. 118*a*).

[2]) Proc. Febr. 1911. Comm. No. 117.

[3]) M. REINGANUM. Diss. Göttingen 1899. Ann. d. Phys. (4). 18. 1008. 1905. Phys. Ztschr. 11. 735. 1910.

[4]) G. VOGEL. Diss. Freiburg (Baden) 1910, Ztschr. f. phys. Chem. 73. 429. 1910.

Botany. — *On the connection between stimulus and effect in phototropic curvatures of seedlings of Avena sativa.* By W. H. Arisz. (Communicated by Prof. F. A. F. C. Went).

At about the same time there appeared in 1908 papers by Blaauw [1]) and by Fröschel [2]) on the perception of lightstimuli.

If a seedling of Avena or Lepidium is unilaterally illuminated, then with different intensities of light a just perceptible reaction was found to take place, when the product of the intensity of light and the duration of the stimulus was a constant.

A repetition of these investigations in Professor Went's laboratory led to some observations of which I here give a preliminary account.

Madame Polowzow [3]) showed for aerotropic and geotropic curvatures, that under the microscope a curvature is seen to occur immediately after the stimulation. Blaauw [4]) discusses to what extent this may also be regarded as probable in the case of phototropic curvatures. He is of opinion, that either the reaction where it has become macroscopically visible must just have begun or that at this moment a new stage in the curvature process has been entered upon, and that therefore in any case he is working, with a definite point of the reaction.

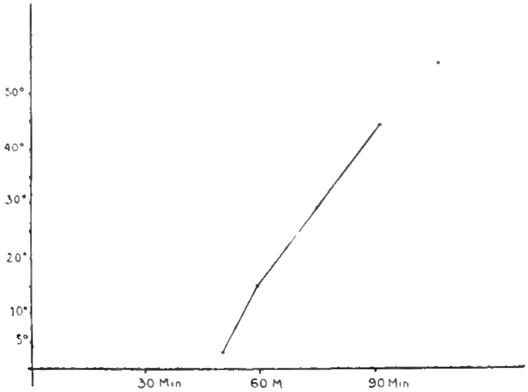

Fig. 1.
Course of the phototropic curvature after Blaauw.
On the abscissa the time in minutes from the beginning of stimulation, on the ordinate the magnitude of the angle of deviation.

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[1]) A. H. Blaauw. Proc. Acad. Sci. Amsterdam, Sept. 1908.

[2]) P. Fröschel. Sitzungsberichte der K. Akad. der Wiss. Wien, April 1908.

[3]) W. Polowzow. Untersuchungen über Reizerscheinungen bei den Pflanzen. 1909.

[4]) A. H. Blaauw. Die Perzeption des Lichtes. Recueil d. Trav. Bot. Néerl. Vol. 5, 1909.

It remains to trace also the course of a phototropic curvature with the microscope in the same way as POLOWZOW did for geotropic curvatures.

In view of the manner of curving, to be described later, the distance between the original position of the tip of the coleoptile and the new position occupied at any moment during the curvature is chosen as the measure of the curvature at that moment. MAILLEFER [1]) and POLOWZOW also took this distance as a measure of the curvature. In the eye-piece there was a net-micrometer, so that it was possible to make under the low power a drawing on squared paper of the whole apex.

By comparing these drawings, made every 5 or 10 minutes, it was possible to trace the origin of a slight alteration in shape. Nutations gave a good deal of trouble, though all specimens in which these occurred were absolutely rejected. Since the nutation movements are sharply distinguished from a phototropic curvature by the change of position of the whole apex with respect to the base, it was fairly easy to recognise them.

In the following curves the abscissa is the time and the ordinate the strength of curvature, measured in the afore-mentioned way.

In one case therefore the curvature began after 12 minutes. Are we then to conclude that the curvature begins just at this moment and that the reaction time is therefore 12 minutes? I think not; it seems to me it would appear that we must come to this conclusion after a study of the shape of the apex at the beginning of the curvature. It is found that while this shape is at first almost exactly conical with a somewhat blunted top, the curvature becomes visible as a slight mutual asymmetry of that side of the cone which is turned towards the light and that which is turned away from it. This asymmetry becomes gradually more marked until the apex begins to bend forward and the curvature extends further and further from the apex. There is no indication of the sudden appearance of curvature. In a few cases the shape of the apex favours the perception of even a slight asymmetry, but it is very probable that in such cases a curvature occurred, even before a deviation was traceable.

The determination of a reaction-time is therefore experimentally impossible, and it is quite conceivable, that the curvature occurs immediately on stimulation.

The passage of a part of the curve which is only visible micro-

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[1]) A. MAILLEFER. Etude sur la Réaction géotropique. Bull. Soc. Vaudoise. 1910.

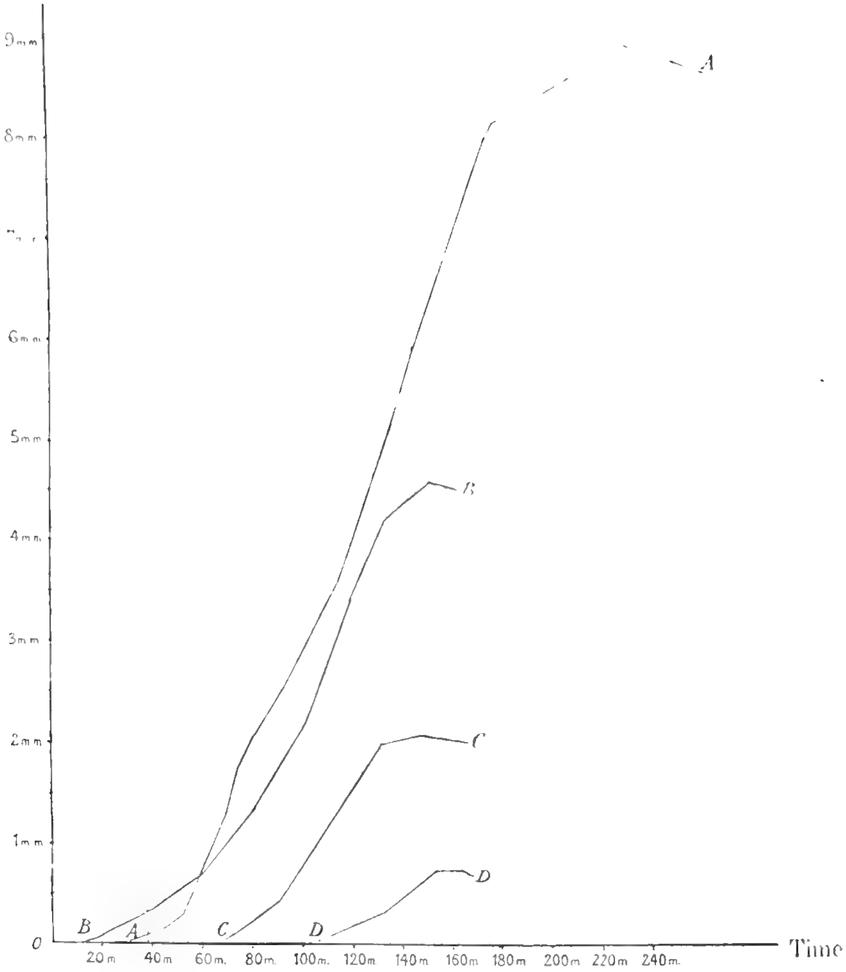

Fig. 2.
Course of the phototropic curvature.
A. stimulated with 800 M.C.S. B. with 112 M.C.S.
C. with ± 20 M.C.S. D. with 5 M.C.S.

scopically into a part which can also be perceived macroscopically, takes place more or less gradually.

An obvious break occurs on strong stimulation (see fig. 2 A). BLAAUW's interpretation, that the curvature here enters on a new phase, seems to me very plausible, when we see that just at this moment the parts remote from the apex, which in contradistinction to the apex itself show a considerable increase in length, begin to take part in the curvature.

On comparison of curves obtained in such a way, it became obvious that the maximum curvature seen in plants which were illuminated with different intensities, was not equally great in every case; with weaker light it was considerably less.

It was found that slighter curvatures exist than those observed by BLAAUW and by FRÖSCHEL. This was a quite unexpected result, for although BLAAUW had very cautiously spoken of those curvatures which were only just macroscopically visible, he still believed he was working with a threshold of stimulation.

This applies still more to FRÖSCHEL, who attached great value to the smallest product still giving a curvature, as a measure of phototropic sensitiveness, for comparison with that of other plants.

Has the deviation of the apex valued by BLAAUW as still showing curvature, any special value, to which alone the rule of products applies, or would it be found, that to a smaller or greater energy of stimulus there also corresponds a smaller or greater curvature? In general, that a definite quantity of energy causes a definite extent of curvature?

In order to obtain an answer to this question a larger number of experimental data had to be available.

The tedious observation with the microscope was superseded by a much simpler apparatus. A photographic lens, magnifying 2 times, projected the image of the seedlings on a glass plate, upon which a scale of half-millimetre squares had been photographed. The position of the apices was read by means of a simple lens.

The advantage of this arrangement is that in addition to a greater number of plants, the whole coleoptile can always be observed. The deviation of the apex from its original position before the beginning of the curvature, chosen at the moment when this distance is greatest, was taken as the measure of the magnitude of the curvature. Since from the beginning gravity opposes the curvature, there comes a moment when the apex under the influence of phototropism moves no further from the vertical, because phototropism is neutralised by gravity. Although this point will probably give no accurate idea of the sensitiveness, it is here only necessary to have a fixed point of the curvature-proces.

Out of many observations made, I here bring together the following, which hold good for seedlings of an average length of 22.5 m.m. at a temperature of about 17.5 degrees Cent.

The light energy was obtained by various combinations of intensities by stimulation periods of various lengths. (from 2 to 240 sec.)

The intensities were determined by a WEBER [1]) Photometer.

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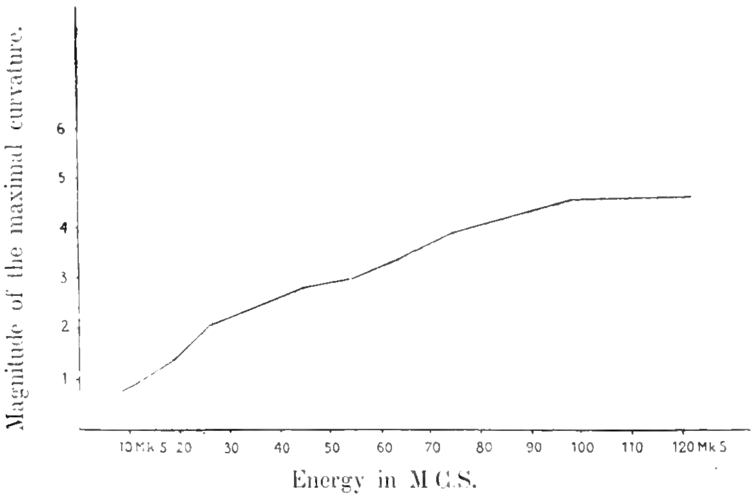
[1]) Prof. H. SNELLEN, Director of the Dutch Eye Hospital was kind enough to place this photometer at my disposal.

Light energy in M.C.S. [1]	Magnitude of the maximal curvature in mm.	Number of observations
7.6	0.73	12
12.4	0.96	6
18.1	1.47	10
26.1	2.1	6
44.2	2.8	15
54.0	3.0	7
65.0	3.4	16
75.3	3.9	7
99.0	4.6	13
126.6	4.6	11
144.0	4.3	10
239.0	4.9	10
576.0	3.6	13

These figures are found to be on a smooth curve, which therefore represents the relation of energy and maximal curvature.

Fig. 3.



The curve gives the relation of light energy used as a stimulus and the magnitude of the maximal curvature for plants of ± 22.5 mm. length and a temp. of 17.5° Cent.

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[1] M.C.S. Means the product of the intensity of the light (in Meter candles) and of the length of the exposure.

Up to 100 M.C.S. there was an increase in the magnitude of the curvature, at first more rapid and then somewhat lower; from 100 M.C.S. to 400 M.C.S. the same magnitude, after which there is a decrease. Below 7 M.C.S. the curvature could not be measured by this method, up to 2 M.C.S. the curvature, as a faint inclination of the apex, was still clearly visible macroscopically. These apical inclinations have been noticed before, e.g. by RUTGERS[1]), who did not however recognise them as phototropic curvatures, because they also arose without previous stimulation. Control-experiment which I made, showed however that when coleoptiles, which showed absolutely no inclination of the apex, were placed in the dark and care was taken that they were previously stimulated neither geotropically nor mechanically by touch or similar agency, they showed no apical inclination, whereby, however (RUTGERS l. c. p. 56) attention was only paid to the curvature at right angles to the plane of nutation.

Below 2 M.C.S. the curvature was so faint, that macroscopically it could not be recognised with certainty. The microscope is likewise inadequate for this. The smallest curvature observed was about $^1/_4$ mm. at 1.4 M.C.S.

No limit can therefore be fixed below which no curvatures arise, but that there are curvatures which at present escape our observation, is highly probable. The suggestion is obvious, and the course of the curve is an argument in favour, that the curve should be continued to point 0. The significance of this is, that every quantity of energy gives rise to a definite degree of curvature.

Each quantity of energy reacts on the plant and is expressed by a curvature of definite maximal strength.

Since the phototropic curvatures with which these observations are concerned, were all to some extent counteracted by gravity, it was desirable to have for comparison experiments, from which the unilateral action of gravity had been eliminated. For this purpose Fitting's intermittent clinostat was used, which makes it possible to place a plant during equal intervals alternately in positions which differ from one another by 180 degrees, so that the action of gravity in one position balances that in the other. In 2 minute periods no appreciable curvature arose in unilluminated plants after 6 hours. Out of every 4 minutes the plants were for 2 minutes in a position in which they could be examined and drawn under the microscope.

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[1]) A. A. L. RUTGERS, De invloed der temperatuur op den praesentatietijd bij geotropie. Dissertatie, Utrecht 1910.

The curve below gives the course of a curvature of this kind.

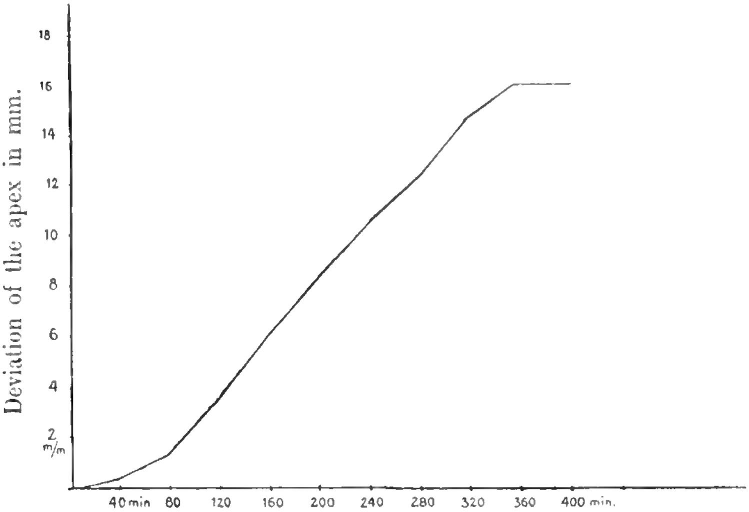

Fig. 4.

Course of the phototropic curvature whilst the unilateral action of gravity is eliminated. Stimulated with 360 M. C. S.

It is clear from this curve that already after 10 minutes, sooner therefore than when gravity is opposing, a curvature becomes visible; this is of course a strong argument in favour of an earlier beginning of the curvature-process. After about 6 hours there comes a moment in which the distance from the vertical no longer increases. In order to facilitate a survey of the curvature I here reproduce figures made from drawings on frosted glass by outlining the image projected by the photographic lens.

If one compares with this a curvature in which gravity opposes, the great difference is at once striking. In this case too, first the becoming asymmetric of the apex, after which the curvature affects more and more basal zones. After about 6 hours the greatest deviation of the apex is reached. If the strength of the curvature is determined at this moment by placing arcs of different radius along the curved part, it is found that the coleoptile is not bent in the arc of a circle but consists of a series of parts with different degrees of curvature. Thus the zone situated fairly close to the apex is most strongly curved, perhaps because it is the zone of most active growth. After these 6 hours the curvature of the uppermost part decreases, so that a slight diminution of the deviation of the apex is observable; it is the beginning of the straightening out. In the more basal parts the curvature still increases continuously. Finally the whole upper part

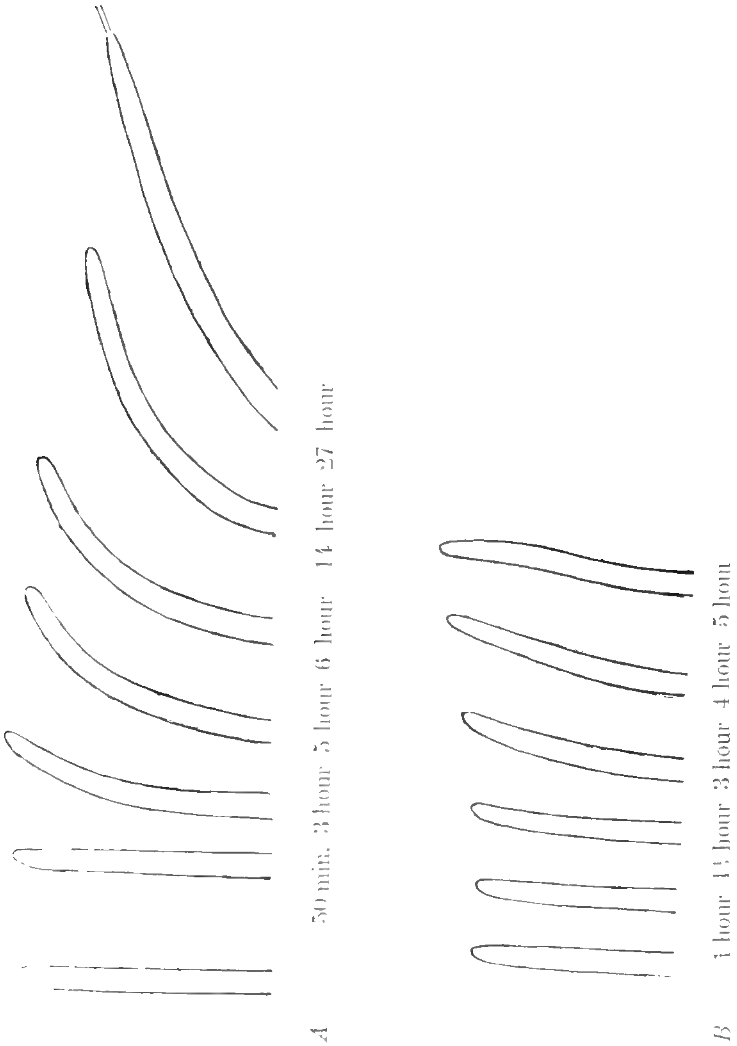

Fig. 5.

A. The course of the curvature whilst the unilateral action of gravity is eliminated.
B. The course of the curvature whilst the unilateral action of gravity is not eliminated.
A and *B* stimulated by the same quantity of light + 25 M.C.S. (2 ×).

becomes straight and the curvature in the base has become fixed.

Perhaps we possess therefore in this method of observation with an intermittent clinostat a more accurate means of determining the sensitiveness of the plant.

If we once more trace how far the above investigations influence our conception of the process of stimulation, it is clear that the comparability with physico-chemical processes becomes more and more marked. The existence of a threshold of stimulation can no longer be maintained, for not only is each quantity of energy perceived but it is clear now that a reaction will always take place. The time which intervenes between the application of the stimulus and the beginning of the curvature, "the reaction-time" was found to be experimentally undeterminable. Thus the latter can not serve as a measure of sensitiveness.

It is more and more evident that such concepts as "Erregung" and "Erregungshöhe" can be perfectly well dispensed with, because the phenomena do not give the slightest indication of their use.

Similarly the determination of an index or time of relaxation will be found impossible, because it is impossible to show experimentally that no curvature results from the summation of intermittent stimuli.

Since the presentation-time has been conceived as a factor of the quantity of energy, which is just able to traverse the threshold of stimulation, it follows from the above investigations, that when the "Schwelle" is abandoned the presentation-time loses much of its value as a special stimulation period. It remains however, as a time factor of the quantity of energy, which results in a curvature of definite strength.

Henceforth therefore the physiology of stimulation must be investigated by considering the energy which is applied as stimulus and which is determined by the product of the intensity of the operating force and the length of the stimulation period, whilst the reaction can be gauged by the degree of the maximal curvature, at least if the unilateral action of gravity is not eliminated. If the latter be

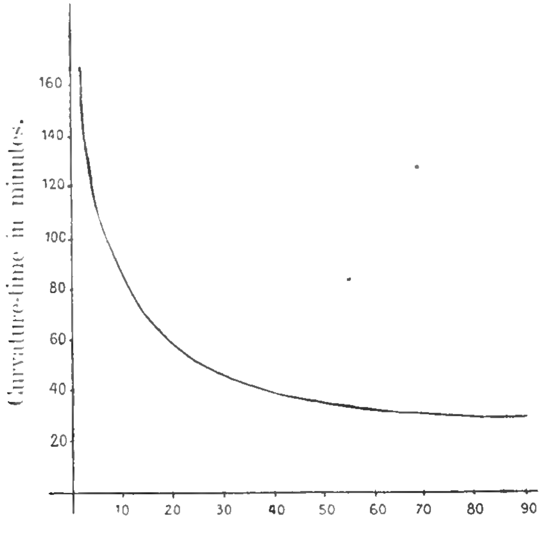

Fig. 6.

Relation between Energy and the time untill the curvature becomes just macroscopically visible.

eliminated the degree of curvature at the moment when straightening out begins, can perhaps serve as measure.

If one wishes to investigate the influence of some external condition on the sensitiveness, one can determine what quantity of energy gives a definite degree of curvature each time this condition is varied; in which case it is very convenient that the moment at which such a curvature becomes visible, is constant.

What was formerly understood by reaction-time but what has now been found to be almost exclusively *curvature-time*, is *constant* for a definite quantity of energy. This curvature-time greatly increases according as the energy of stimulation is smaller, a fact clearly shown by the following curve.

In conclusion I wish heartily to thank Dr. BLAAUW and in particular Professor WENT for their kind interest and advice.

Utrecht. Bot. Laboratory.

Crystallography. — "*On the orientation of crystal-sections.*" By J. SCHMUTZER. (Communicated by Prof. C. E. A. WICHMANN).

(Communicated in the meeting of February 25, 1911).

When determining the orientation of a secant-plane from the angles that the traces of three unparallel planes not lying in one zone include together, one generally obtains a biquadratic equation in *cos* 2ϱ, furnishing as maximum 4 compatible roots. As now angle 2ϱ can be supposed at the same time in two quadrants, it follows that one finds 8 values for ϱ. With these values correspond 8 values of σ. If however three crystal-planes and a definite crystal-section are given, the secant-plane is entirely determined; which value of ϱ and of σ comes in consideration here, can be decided with certainty, if one takes into account the circumstance that a crystal-plane is at the same time the boundary-plane of the mineral substance.

Being admitted a plane (hkl) (cf. fig. 1) the pole of which lies in p, and forming with the plane C ($\perp$ c-axis) a secant-line AB, then the angle $DBE = \alpha < \frac{\pi}{2}$ is filled with mineral-substance, the obtuse angle EBI on the contrary is not. Now one can suppose the projection-globe divided into 8 octants of which 4 are lying above and 4 beneath the projection-plane C, and of which the first two ($BOD =$ I, $DOA =$ II) contain the acute plane-angle DBE. If one fastens s to the coordinates $\varrho = \frown BM$, $\sigma = \frown Ms$, then s lies in the 1st globe-octant, calculated from AB; for a plane $P'' (\bar{h}\bar{k}l)$ s lies in octant III.

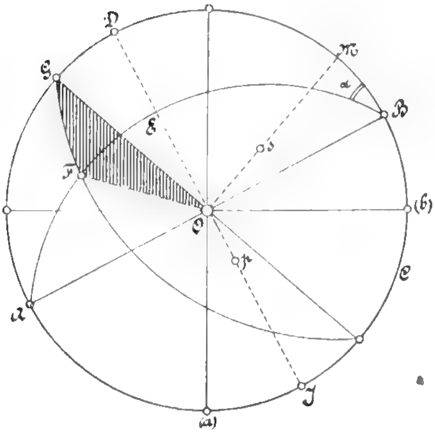

Fig. 1.

The plane S cuts $P(hkl)$ according to the line FO; the mineral substance lies to the right of this secant-line, as is indicated by the hatching. If with a constant value of $\sigma\ (\sigma = \sigma_1)$, ϱ increases, then the angle $h = \angle\, GOF$, which for $s\ (\varrho, \sigma)$ in the first octant > 0 and $< \frac{\pi}{2}$, diminishes, till with $\varrho = \frac{\pi}{2}$ the value $h = 0$ is reached

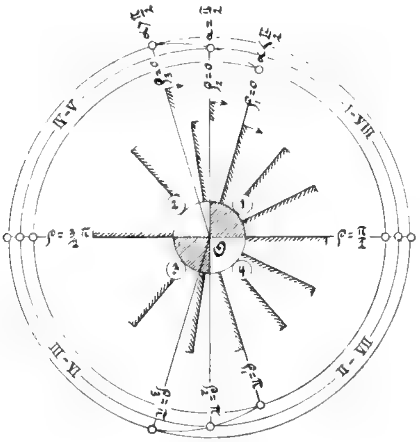

Fig. 2.

Now becomes $h < 0$, obtains in the IIIrd octant a value $-\frac{\pi}{2}$; with $\varrho = \frac{3}{2}\pi$ is $h = -\pi$; in the IVth octant the value $h = -\frac{3}{2}\pi$ is surpassed; and at last with $\varrho = 2\pi$ h obtains the value $-2\pi + h_0$, in which h_0 is the angle, that corresponds to $\varrho = 0$, $\sigma = \sigma_1$.

Fig. 2 represents the change of angle h for a plane $V\ (\alpha = 60^\circ)$, in which ϱ increases with 30° and $\sigma = 60°$. For $\varrho_1 = 0$ $h = 73°54'$; with increasing ϱ_1 h diminishes, becomes $= 0$ with $\varrho_1 = \frac{\pi}{2}$, $= -73°54'$ with $\varrho_1 = \pi$, $= -\frac{\pi}{2}$ with $\varrho_1 = 199°28'$ and reaches the value of $-2\pi + 73°54'$ with $\varrho_1 = 2\pi$.

It is further indicated in the figure, that with equal absolute values of ϱ and σ h is identical in the octants I and VIII, II and VII, III and VI, IV and V. In the central circle it is likewise indicated, that the cotangent in the quadrants 1 and 3 > 0, in 2 and 4 < 0. Now, as may be deducted from the diagrams fig. 4, 5 in the former communication, with $\alpha < \frac{\pi}{2}$ h varies for different values of ϱ and σ, in the octants I and VIII exclusively between 0 and $\frac{\pi}{2}$, in II and VII between 0 and $-\frac{\pi}{2}$. In fig. 2 consequently the octants I and VIII resp. II and VII never extend over the quadrants 1 and 3; the octants IV and V however do so over quadrant I and III and VI over 4. Consequently if one finds from the ratio

$$cot\, h = \frac{cos\, \sigma\, cot\, \alpha + sin\, \sigma\, sin\, \varrho}{cos\, \varrho}$$

$cot\, h > 0$, then h must be admitted in the first quadrant, if $s\,(\varrho, \sigma)$ lies in one of the octants I, IV, V or VIII, and in the 3rd quadrant if s lies in III or VI. If $cot\, h < 0$, then h lies in the 2nd quadrant with s in IV or V, and in the 4th if s lies in the IInd or VIIth octant.

As regards the planes with $\alpha = \frac{\pi}{2}$ and $\alpha > \frac{\pi}{2}$ the figure speaks for itself. Consequently the results obtained here may be summarised in the following table:

	$cot\, h > 0$								$cot\, h < 0$							
	I	II	III	IV	V	VI	VII	VIII	I	II	III	IV	V	VI	VII	VIII
$\alpha < \frac{\pi}{2}$	1	—	3	1	1	3	—	1		4	4	2	2	4	4	
$\alpha = \frac{\pi}{2}$	1	—	3	—	—	3	—	1	—	4	—	2	2	—	4	—
$\alpha > \frac{\pi}{2}$	1	3	3	—	—	3	3	1	2	4	—	2	2	—	4	2

Of a trigonal prism are given the planes V_1 $(0\bar{1}10)$ and V_2 $(10\bar{1}0)$, further V_3 (0001). If one admits the latter plane as projection-plane, then becomes $\alpha_1 = \alpha_2 = \frac{\pi}{2}$; $\gamma = 120°$.

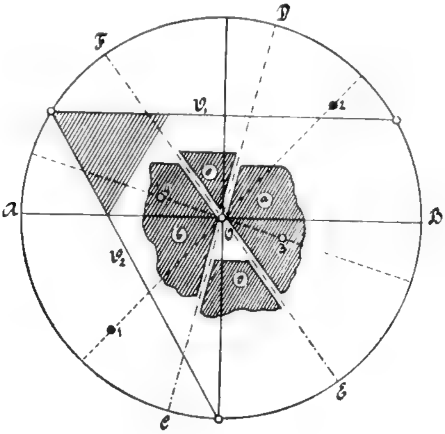

Fig. 3.

If further one measures between the traces of $V_1 : V_3$ and $V_2 : V_3$ successively the angles $h_1 = 76°$, $h_2 = -53°$, then furnishes (1)

$$cot\ 76° = sin\ \sigma\ tg\ \varrho$$

and

$$cot\ 53° = -\ sin\ \sigma\ tg\ (\varrho - 120°)$$

from which:

$$tg^2\ \varrho - \frac{cot\ 76° + cot\ 53°}{tg\ 60°\ cot\ 53°}\ tg\ \varrho - \frac{cot\ 76°}{cot\ 53°} = 0$$

$$tg\ \varrho = 1{,}07592 \quad \text{of} \quad -\ 0{,}30754.$$

From this the values are found:

$\varrho_1 = 47°5'58''$; $\varrho_2 = -132°54'2''$; $\varrho_3 = +\ 162°54'17''$; $\varrho_4 = -\ 17°5'43''$
$\sigma_1 = 13°33'49''$; $\sigma_2 = 13°33'49''$; $\sigma_3 = -\ 54°9'53''$; $\sigma_1 = -54°9'53''$.

Be in fig. 3 AB the trace of V_3 (0001), then

$$CD\ (\angle\ DOB = h_1 = 76°)\ \text{and}\ EF\ (\angle\ BOE = h_2 = -53°)$$

indicate the direction of the traces of V_1 and V_2. The plane S_1 $(\varrho_1\ \sigma_1)$ has its pole with regard to V_1 in octant I, $coth_1 > 0$, h_1 consequently lies in quadrant 1; with regard to V_2, s_1 lies in octant IV, $coth_2 < 0$, h_2 in quadrant 2, whilst $h_3 = 0$, and the trace of V_3 consequently shuts off the section at the top. Consequently the section a corresponds to the secant-plane S_1; in the same way one finds, that the sections b, c, and d have relation to the secant-planes S_2, S_3, and S_4. And in this way a choice between the four poles found has become possible with certainty.

If the orientation of the crystal discussed here, must be determined with the help of 2 crystal-planes and one cleavage-plane, then two solutions remain satisfactory, as is easily seen, whilst with 1 crystal-plane and two cleavage-planes, or likewise with 3 cleavage planes all 4 solutions may be taken into consideration.

Cristallography. — *"On the determination of the optic axial-angle from the extinction-angle with regard to the trace of a discretional plane in a discretional crystal-section"*. By J. Schmutzer (Communicated by Prof. C. E. A. Wichmann).

(Communicated in the meeting of February 28, 1911).

Be in fig. 1 the projection-plane perpendicular to the bisectrix of the optic-axes, A and B and be further $S(s)$ the secant-plane, then the directions of the vibration in the slide are given by the planes that halve the angle AsB and its supplement.

Be angle x the inclination of the bisectrix (O) on the secant-plane S; $\angle IKMH = \alpha$ the angle, enclosed by the secant-lines of the planes AOB and S with the projection-plane, then, as was

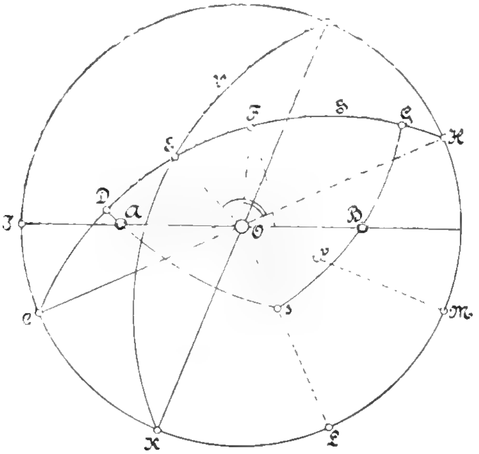

Fig. 1.

deducted before, in the plane S the extinction with regard to the secant-line OH can be found from the equation:

$$\cot 2y = \cot 2 \frown FH = \cot (\frown DFH + \frown GH) =$$

$$= -\frac{1 - \sin^3 V \sin^2 \alpha}{\sin 2\alpha \,.\, \sin^3 V} \cdot \frac{1}{\sin x} + \frac{1 - \sin^2 V \cos^2 \alpha}{\sin 2\alpha \sin^2 V} \sin x \quad . \quad . \quad (1)$$

If the pole s of S is fastened to the coordinates $\varrho = \frown IKL$, $\sigma = \frown Ls$, then (1) changes into

$$\cot 2y = \frac{1 - \sin^2 V \cos^2 \varrho}{\sin 2\varrho \sin^2 V} \cdot \frac{1}{\sin \sigma} - \frac{1 - \sin^2 V \sin^2 \varrho}{\sin 2\varrho \sin^2 V} \sin \sigma =$$

$$= \frac{1 - \sin^2 V \cos^2 \varrho - (1 - \sin^2 V \sin^2 \varrho) \sin^2 \sigma}{\sin 2\varrho \sin \sigma \sin^2 V} \quad . \quad . \quad . \quad (2)$$

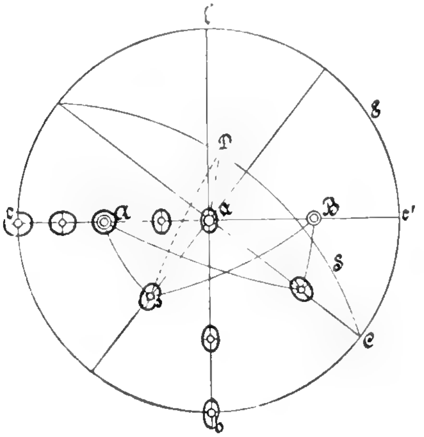

Fig. 2.

To every value of *cot* $2y$ correspond two values of y, which differ 90° from each other, and which indicate the direction of the vibration of the quick ray resp. of the slow one. Without more the direction of each of the ellips-axes cannot be deduced from the formula; to find it afterall, one acts in the following way. In fig. 2 the globe-octants cab, bac', c'ab' and b'ac be indicated by the figures I, II, III and IV in so far as they are above, and, by V, VI, VII, VIII in so far as they lie below the projection-plane. In the first octant ϱ varies between 0 and $\frac{\pi}{2}$ $\sin 2\varrho > 0$; σ between 0 and $\frac{\pi}{2}$, $\sin \sigma > 0$.

The sign of *cot* $2y$ in the formula (2) is consequently entirely defined by the sign of the numerator of the fraction.

$\cot 2y = 0$, if $(\sin 2\varrho \sin \sigma \sin^2 V > 0)$:

$$(1 - \sin^2 V \cos^2 \varrho) - (1 - \sin^2 V \sin^2 \varrho) \sin^2 \sigma = 0.$$

If, with a constant value of σ and V, ϱ increases, then the formula becomes:

$$1 - \sin^2 V \cos^2 \varrho - (1 - \sin^2 V \sin^2 \varrho) \sin^2 \sigma =$$

$$= 1 - \sin^2 \sigma (1 - \sin^2 V) - \sin^2 V (1 + \sin^2 \sigma) \cos^2 \varrho \quad . \quad . \quad (3)$$

by the diminution of $\cos\varrho > 0$ and becomes with $\varrho = \frac{\pi}{2}$

$$\cot 2y = \frac{1 - \sin^2\sigma\,(1 - \sin^2 V)}{(\sin 2\varrho = 0)\,\sin\sigma\,\sin^2 V} = +\infty.$$

From this follows:

$$2y = \pm\, 180^\circ \text{ or } 0^\circ$$

$$y = \pm\; 90^\circ \text{ or } 0^\circ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad 4$$

In fig. 2 the $\mathfrak{a}$-axis has been chosen as normal to the projection-plane; it needs no further elucidation, that the plane that halves $\angle AsB$, here always indicates the direction of the vibration of the quicker ray. If the pole of the secant-plane lies in the plane $\mathfrak{b}\mathfrak{b}'$, then y_a, the angle between the longer ellipse-axis and the secant-line $S : E (= \mathfrak{a}')$ becomes $= \frac{\pi}{2}$, so that the value $y = 0 = y_c$ relates to the short ellipse-axis.

If consequently the projection-plane is placed ⊥ to the negative bisectrix, one finds with the help of (2) the angle, that the long axis of the ray-velocity-ellipse forms with the secant-line of the projection-plane and the secant-plane, if with a positive value of $\cot 2y$ one takes the angle $2y_a$ in the 3rd quadrant. Then y_a is likewise an angle in the 2nd or 4th quadrant, and has consequently, if we take the value $< \frac{\pi}{2}$, a negative sign.

If in the 1st octant ϱ diminishes from the point where with a definite value of σ and V

$$1 - \sin^2\sigma\,(1 - \sin^2 V) - \sin^2 V\,(1 + \sin^2\sigma)\cos^2\varrho = 0$$

then, in consequence of the increase of $\cos\varrho$, the formula (2) has negative values. With $\varrho = 0$ becomes:

$$0 > \cot 2y = \frac{1 - \sin^2 V - \sin^2\sigma}{(\sin 2\varrho = 0)\,\sin\sigma\,\sin^2 V} = \frac{\cos^2\sigma - \sin^2 V}{(\sin 2\varrho = 0)\,\sin\sigma\,\sin^2 V}.$$

If now one assumes for σ all values between 0 and $\frac{\pi}{2}$, then it appears, that $\cot 2y_a$ becomes indefinite for

$$\cos\sigma = \sin V = \cos\left(\frac{\pi}{2} - V\right).$$

The pole of the second plane lies here in the optic-axis. For $\sigma > \frac{\pi}{2} - V$, $\cos^2\sigma - \sin^3 V$ becomes < 0, by which $\cot 2y$ obtains a positive value, and $2y$ must be supposed in the 3rd quadrant;

$\cot 2y = +\infty$, $y_a = \pm 90°$. For $\sigma < \frac{\pi}{2} - V$ $\cos^2\sigma - \sin^2 V$ becomes > 0, $\cot 2y < 0$ i. e. $-\infty$: the angle $2y$ in accordance with the figure must, be taken in the 4th quadrant: $2y_a = 0°$, $y_a = 0°$.

For $\frac{\pi}{2} > \varrho > 0$ and $\cot 2y < 0$ consequently $2y_a$ lies in the 4th quadrant, and y_a, in so far as one takes the value $\frac{\pi}{2} > y_a > -\frac{\pi}{2}$ likewise in the 4th quadrant. In the 1st octant consequently is always $-\frac{\pi}{2} < y_a < 0$. The same holds good for the octants III, VI and VIII, where the denominator of the formula (2) is likewise > 0.

To the value $y_a(\varrho,\sigma)$ in the first octant correspond identical values with $(\pi + \varrho)$, σ in the IIIrd, $(\pi - \varrho)$, $-\sigma$ in the VIth, and $(2\pi - \varrho)$, $-\sigma$ in the VIIIth octant. Where the product $\sin 2\varrho \sin \sigma < 0$ (cf. (2)), consequently, in the IInd, IVth, Vth and VIIth octant becomes $0 < y_a < \frac{\pi}{2}$. To $y_a(\varrho,\sigma)$ in the 1st octant correspond identical values with a contrary sign with ϱ, $-\sigma$ in the Vth, $(\pi - \varrho)$, σ in the IInd, $(\pi + \varrho)$, $-\sigma$ in the VIIth, and $(2\pi - \varrho)$, σ in the IVth octant. In the same way as has been done above for the octants I, III, VI, and VIII one can determine the ratio between the sign of $\cot 2y$ and the value of y_a. The following result is obtained: if the z-axis stands perpendicular to the projection-planes, then lies

$$\left.\begin{array}{lll}
\text{in the octants I, III, VI, VIII} & & \\
\qquad\qquad \text{with } \cot 2y > 0, & 2y_a \text{ in the 3rd quadrant} \\
\qquad\qquad \phantom{\text{with }} \cot 2y < 0, & 2y_a \text{ in the 4th quadrant} \\
\text{in the octants II, IV, V, VII} & & \\
\qquad\qquad \text{with } \cot 2y > 0, & 2y_a \text{ in the 1st quadrant} \\
\qquad\qquad \phantom{\text{with }} \cot 2y < 0, & 2y_a \text{ in the 2nd quadrant}
\end{array}\right\} \quad (4^a)$$

In this way the orientation of the velocity-ellipse can be found with certainty.

To find the angle which, in a discretionary section, the long ellipse-axis forms with the trace of a discretionary plane V, we return to fig. 1. The plane V, the pole of which is given by the coordinates $\mu = \frown HLM$, $\nu = \frown M\nu$, is cut by S according to the line EO, forming with OH an angle $H\dot{O}E = h$. Now we found that

$$\cot h = \frac{\cos\sigma \cot\alpha + \sin\sigma \sin(\varrho - \gamma)}{\cos(\varrho - \gamma)}$$

in which $\gamma = \frown ICK = \mu - \frac{\pi}{2}$

$\alpha =$ the angle between Γ and the projection-plane $= r + \frac{\pi}{2}$

so that

$$cot\,h = \frac{cos\,\sigma\,cot\left(r + \frac{\pi}{2}\right) + sin\,\sigma\,sin\left(\varrho - \mu + \frac{\pi}{2}\right)}{cos\left(\varrho - \mu + \frac{\pi}{2}\right)}$$

$$= \frac{cos\,\sigma\,tg\,r - sin\,\sigma\,cos\,(\varrho - \mu)}{sin\,(\varrho - \mu)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

The angle between the long ellipse-axis and the trace of Γ is consequently given by

$$\angle FOE = \angle HOF - \angle HOE = y_a - h \quad . \; . \; . \; . \; . \quad (6)$$

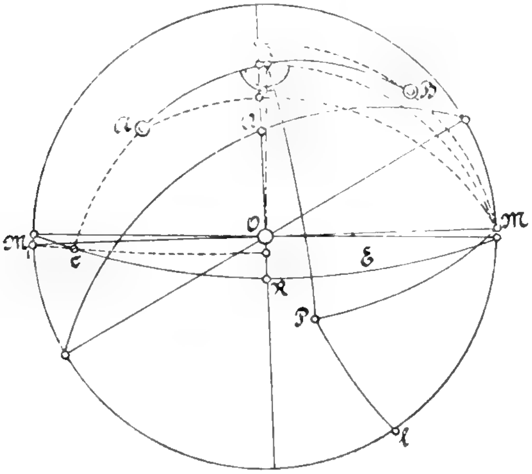

Fig. 3.

Fig. 3 gives the projection of a triclinic crystal, oligoclase of Bamle [1]. If one measures ϱ along the great circle ROQ from the plane MOM_1 positively opposite to the hands of a clock, σ from ROQ positively to the right, then the optic-axes A and B and their bisectrices are determined by:

	ϱ	σ
A	$-67°58'$	$-44°58'$
B	$-83°53'$	$+47°9'$
$\mathfrak{a}$	$-75°36'$	$+1°6'$
$\mathfrak{c}$	$+6°35'$	$-82°28'$

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[1] Rosenbusch, Mikrosk. Physiogr. I. 2, 342.

In $\angle ABM$ is $AB = 2V$; $AM = 134°58'$; $BM = 42°51'$; $\angle BMA = 15°55'$; from this follows $2V = 93°10'30''$; $V = 46°35'15''$.

The extinction-angle with regard to the trace of $P(001)$ in the secant-plane $M(010)$ is calculated as follows. If one takes ⊥ to the bisectrix $O\mathfrak{a}$ a plane E, corresponding to the projection-plane in fig. 1, one finds for the planes $M (= S)$ and $P (= V)$ the following coordinates of the poles:

$$\left.\begin{aligned} \varrho &= \angle A\mathfrak{a}M = 2\pi - \angle B\mathfrak{a}M = 172°58' \\ \sigma &= \frac{\pi}{2} - \frown M\mathfrak{a} = 1°6' \end{aligned}\right\} \quad . \quad . \quad . \quad (7)$$

$$\mu = \angle A\mathfrak{a}P \quad \text{and} \quad \nu = \frac{\pi}{2} - \frown P\mathfrak{a}$$

In order to find μ and ν one proceeds from the given equations:

$$M : P = 86°32'; \; M : l = 59°14'; \; P : l = 65°40'.$$

From these one calculates:

$$\angle PMl = 63°37'; \; \angle OMP = \frac{\pi}{2} - 63°37' = 26°23';$$

$$\angle \mathfrak{a}MP = 26°23' + 75°36' = 101°59':$$

so that now from $\angle \mathfrak{a}MP$ can be found:

$$\frown \mathfrak{a}P = 101°53'20'' \quad \text{and} \quad \nu = -11°53'20'' \quad . \quad . \quad . \quad (7a)$$

Further one finds:

$$\begin{aligned} \angle M\mathfrak{a}P = 86°13'; \; \mu = \angle A\mathfrak{a}P = 2\pi - (\angle M\mathfrak{a}P + \angle B\mathfrak{a}M) = \\ = 2\pi - (86°13' + 7°2') = 86°45'. \quad . \quad . \quad . \quad . \quad (7b) \end{aligned}$$

The planes M and E $(\perp \mathfrak{a}O)$ cut each other according to the line OR; with regard to this line the extinction in M amounts to an angle y given by (cf. (2)):

$$\cot 2y = -\frac{1 - \sin^2 V \cos^2 7°2' - (1 - \sin^2 V \sin^2 7°2') \sin^2 1°6'}{\sin 14°4' \sin 1°6' \sin^2 V}$$

$$\lg \cot 2y = 2,28980\,(-).$$

and as the pole of M ($\varrho = 172°58'$, $\sigma = 1°6'$) lies in the II$^{\text{nd}}$ octant $2y_a$ must be taken in the 2$^{\text{nd}}$ quadrant, so that

$$2y_a = 180° - 17'38''$$

$$y_a = \frac{\pi}{2} - 8'49'' = + 89°51'11''. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The angle that the trace of P makes with the direction OR is found from (5)

$$\cot h = -\frac{\cos 1°6' \operatorname{tg} 11°53'20'' + \sin 1°6' \cos 86°13'}{\sin 86°13'}$$

$$\lg \cot h = 9.32678\,(-)$$

$$h = -78°1'7'' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The angle between the long ellipse-axis and the trace of P is consequently given by (cf. 6)

$$g_a - h = 89°51'11'' + 78°1'7'' \quad 167°52'18'' = -12°8'.$$

Rosenbusch gives (vide above) for the same mineral as calculated value (—) 12°16′.

The method of calculation followed above. is the base for the graphical method, according to which, in a discretional crystal-section the extinction-angle with regard to the trace of a discretional-plane can be determined from the size of the axis-angle. One proceeds, for doing so, from the coordinates μ, r of (V) and φ, σ of (S). If we take the oligoclase discussed above, we find, in the way as was explained last time, the value h in the diagram for $\alpha = \frac{\pi}{2} + r = 78°$ of $\varphi_t = \frac{\pi}{2} + \angle MaP = 176°13'$, $\sigma_t = 1°6'$. As

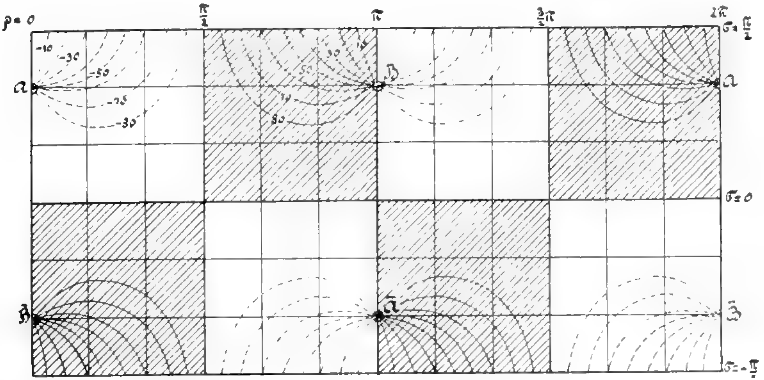

Fig. 4.

appears from the scheme of the h-diagram [1]) a value $h = -\alpha$ corresponds to a secant-plane ($\varphi_t = 2\pi$, $\sigma_t = 0$); one finds consequently likewise in our case for h a value, deviating but little from $-78°$. To determine the optic extinction with regard to the fictive trace of the plane E ($\perp aO$), one uses a second diagram, which has been calculated with the help of the ratio (2), and gives for a definite axis-angle the value g as $f(\varphi, \sigma)$. In fig. 4 the g-diagram for $V = 30°$. is represented; in the hatched octants (II, IV, V, VII) g has a positive value, in the others a negative one. For a further explanation of this diagram we may refer to what was said above about the signification of the ratio (2) and to a former communication in which a similar diagram was discussed [2]). The g-diagram for $V = 46°35'$

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[1]) Compare These Proc XIII, p 731. fig. 4—5.

[2]) These Proc. X, p. 375 et seq.

furnishes for $\varrho_y = \angle \mathfrak{A}a\mathfrak{M} = 172°58'$ and $\sigma_y = \frac{\pi}{2} - \angle \mathfrak{M}a = 1°6'$ about the value $y = +89°50'$. Thereby the value $u = y - h = 12°10'$ is found.

Per contra the axial angle $2V$ can be determined, if one knows the secant-plane $S(\varrho, \sigma)$, the extinction u with regard to the trace of a known plane $V(u, v)$ and the direction of the extreme ray-velocities.

In fig. 5 the amphibole-crystal is represented, of which in the previous communication[1]) with the help of the apparent angles between the prism-planes and the clinopinakoïd the orientation was determined. The angles $\alpha_1 = 55°50'$ and $\alpha_2 = -62°5'$ are here inclosed either by the planes $m_2 : m_1 (= \alpha_1)$ and $b_1 : m_1 (= \alpha_2)$, m_1 taken as equatorplane, or by $m_3 : m_2 (= \alpha_1)$ and $b_2 : m_2 (= \alpha_2)$, m_2 considered as equatorplane[2]). For the place of the poles of the secant-planes S_1 and S_2 found, it does not make any difference, whether m_1 with its pole D, or m_2 with its pole L is taken as equatorplane, as this occasions only an interchange of s_1 and s_2. If one takes m_1 as equatorplane, then lies

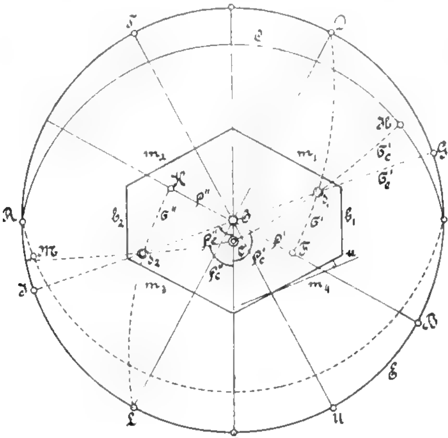

Fig. 5.

$$s_1 \text{ with } \varrho' = \frown OF = 35°5'$$
$$\sigma' = \frown Fs_1 = 30°55'$$
$$s_2 \text{ with } \varrho'' = \frown OK = -35°5'$$
$$\sigma'' = \frown Ks_2 = -30°55'$$

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[1]) These Proc. XIII, p. 728.

[2]) The complications resulting for the orientation from the crystal-symmetry will be treated in a further communication.

The extinction observed under these circumsiances amounts with regard to the trace of m_2 (m_1) to $u = -6°$. The plane of the optic-axes OA lies // (010); be further the angle $c : \mathfrak{c} = 10°$, then the axial-angle can be calculated.

For the poles s_1 and s_2 one finds by calculation the following coordinates with regard to the plane-systems OA, E (= projection-plane) and OA, C ($\perp$ bisectrix $\mathfrak{c}$):

$$\frown ABG = \varrho'_e = 108°15'38'' \qquad \frown ALI = \varrho''_e = -\ 71°44'22''$$

$$\frown Gs_1 = \sigma'_e = 44°35'28'' \qquad \frown Is_2 = \sigma''_e = 44°35'28''$$

$$\angle A\mathfrak{c}s_1 = \varrho'_c = 116°48'13'' \qquad \angle A\mathfrak{c}s_1 = \varrho''_c = -\ 81°46'2''$$

$$\frown Hs_1 = \sigma'_c = 40°44'20'' \qquad \frown Ms_2 = \sigma''_c = 46°53'35''$$

For the pole T of the plane m_2 one finds from $\mu_e = \frown ABDT = 2\pi + 27°\,55'$, $r_e = 0$ by calculation $\mu_c = 2\pi + 28°\,16'52''$, $r_c = -\ 8°49'35''$. The angle between the trace of m_2 and the fictive trace of C is according to (5) for the secant-plane S_1

$$cot\ h_1 = \frac{cos\ \sigma'_c\ tg\ r_c - sin\ \sigma'_c\ cos\ (\varrho'_c - \mu_c)}{sin\ (\varrho'_c - \mu_c)}$$

$$= \frac{cos\ 40°44'20''\ tg\ 8°49'35'' - sin\ 40°44'20'\ cos\ 88°31'21''}{sin\ 88°31'21''}$$

from which $h_1 = 84°14'20''$
and for S_2 by:

$$cot\ h_2 = \frac{-\ cos\ 46°53'35''\ tg\ 8°49'35'' - sin\ 46°53'35''\ cos\ 69°57'6''}{sin\ 69°57'6''}$$

from which $h_2 = -\ 69°13'20''$,
so that according to (6):

$$u = y_c - h$$

one finds for S_1 (IInd octant):

$$y'_c = u + h_1 = -\ 6° + 84°14'20'' = 78°14'20''$$

and for S_2 (IVth octant)

$$y''_c = u + h_2 = -\ 6° - 69°13'20'' = -\ 75°13'20''.$$

From the diagram fig. 4 it can immediately be seen, that y for a secant-plane in the IVth octant can never become < 0 and consequently S_2 does not correspond.

Now is according to (2):

$$cot\ 2y = \frac{1 - sin^2\ V\ cos^2\ \varrho - (1 - sin^2\ V\ sin^2\ \varrho)\ sin^2\ \sigma}{sin\ 2\varrho\ sin\ \sigma\ sin^2\ V}$$

$$sin^2\ V\ (cot\ 2y\ sin\ 2\varrho\ sin\ \sigma + cos^2\ \varrho - sin^2\ \varrho\ sin^2\ \sigma) = 1 - sin^2\ \sigma$$

$$sin^2\ V = \frac{cos^2\ \sigma}{cot\ 2y\ sin\ 2\varrho\ sin\ \sigma + cos^2\ \varrho - sin^2\ \varrho\ sin^2\ \sigma} \quad . \quad . \quad . \quad (10)$$

For S_1 becomes:

$$\sin^2 V = \frac{\cos^2 40^\circ 44' 20''}{\cot 23^\circ 31' 20'' \sin 53^\circ 36' 26'' \sin 40^\circ 44' 20'' + \cos^2 63^\circ 11' 47'' - \sin^2 63^\circ 11' 47'' \sin^2 40^\circ 44' 20''}$$

from which

$V = 47^\circ 4'$ round ;; $2V = 58^\circ 52''$ round a as bisectrix.

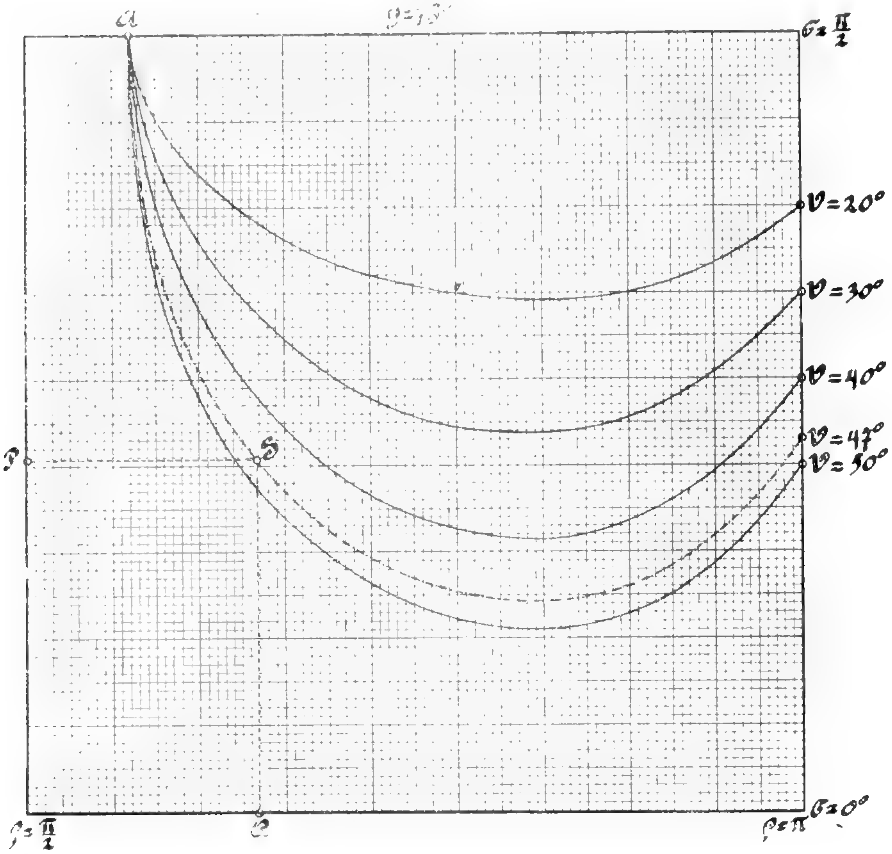

Fig. 6.

From this appears at the same time that the mineral is optically negative.

By a graphical method the axial-angle can easily be determined from η. Fig. 6 gives the curves $\eta = 78^\circ$ for different values of V (comp. fig. 4). In the diagram the pole of $S\,(\rho = 116^\circ 48', \sigma = 40^\circ 44')$ lies between the curves for $V = 40^\circ$ and $V = 50^\circ$, and in a place, which, as appears from interpolation, corresponds to about $V = 47^\circ$. This latter value gives consequently half the axial-angle of the amphibole.

Attention should be paid to the fact that this method furnishes uncertain results, if y differs little from 0° or from $\pm\frac{\pi}{2}$, and consequently the pole of the secant plane lies with a value of ϱ that differs little from $\varrho = 0, \frac{\pi}{2}, \pi$ or $\frac{3}{2}\pi$, or with a little value of σ. With regard to the last condition, one is in a more favourable circumstance with a large axial-angle than with a little one; whilst with $V = 90°$ the curve $y = 89°$ remains in the immediate vicinity of the vertical axes $\frac{\pi}{2}$ and $\frac{3}{2}\pi$ comp. fig. 4) and the horizontal $\sigma = 0$, with $V = 10°$ the corresponding curve does not approach the horizontal $\sigma = 0$ within a latitude of ± 40°.

If y differs little from 0° or $\pm\frac{\pi}{2}$, then $2y$ lies in the vicinity of 0° or $\pm\pi$. In (10) $cot\,2y$ furnishes then, with differences of a few minutes, which cannot be measured with certainty in ordinary circumstances, already values differing so much from one another, that the final result is greatly influenced by it. If we take e.g. the feldspar of Bamle discussed above. For y_a was found the value 89°51′ whilst from the calculation according to Rosenbusch would follow $y_a = 89°43'$.

The difference between $lg\,cot\,2y_a$ and $lg\,cot\,2y'_a$ is

$$2.28100 - 2,00478 = 0.27622,$$

so that here an observation-mistake of 8′ counterbalances 8°35′ with $y = \pm 45°$. Consequently one calculates from the value, given by Rosenbusch for the extinction, with regard to the trace of P (001) in the secant-plane M (010), $u = y'_a$ $h = -12°16'$ (instead of $-12°8'$), a value for $V = 55°50'$ instead of 46°35′). The pole of the secant-plane M, fastened to the axes-plane AB (comp. fig. 3) and the plane $\perp a$, lies with $\varrho = 172°58'$, $\sigma = 1°6'$. So the result was to be expected.

Crystallography. — *"On the determination of an unknown plane from its traces in two orientated crystal-sections."* By J. Schmutzer.
(Communicated by Prof. C. E. A. Wichmann).

(Communicated in the meeting of February 25, 1911).

If one calls the coordinates of the pole of an unknown plane P (crystal-, cleavage- or twinning-plane) μ and ν, if two known secant-planes S_1 and S_2 are given by the poles s_1 (ϱ_1, σ_1) and s_2 (ϱ_2, σ_2) and if further the angles, which the trace of P in these planes makes with the secant-line between secant-plane and projection-plane $(S : E)$ be succ. h_1 and h_2, then

$$cot\, h_1 = \frac{cos\, \sigma_1\, tg\, \mathbf{r} - sin\, \sigma_1\, cos\, (\varrho_1 - \mu)}{sin\, (\varrho_1 - \mu)}$$

$$cot\, h_2 = \frac{cos\, \sigma_2\, tg\, \mathbf{r} - sin\, \sigma_2\, cos\, (\varrho_2 - \mu)}{sin\, (\varrho_2 - \mu)}$$

$$tg\, \mathbf{r} = \frac{cot h_1 sin(\varrho_1 - \mu) + sin \sigma_1 cos(\varrho_1 - \mu)}{cos\, \sigma_1} = \frac{cot h_2 sin(\varrho_2 - \mu) + sin \sigma_2 cos(\varrho_2 - \mu)}{cos\, \sigma_2} \quad (1)$$

from which:

$$cos\, \sigma_2\, \{cot\, h_1\, sin\, (\varrho_1 - \mu) + sin\, \sigma_1\, cos\, (\varrho_1 - \mu)\} =$$
$$cos\, \sigma_1\, \{cot\, h_2\, sin\, (\varrho_2 - \mu) + sin\, \sigma_2\, cos\, (\varrho_2 - \mu)\}$$

which worked out produces:

$$cot\, \mu = \frac{cos \sigma_2 (cot\, h_1 cos\, \varrho_1 - sin\, \sigma_1 sin\, \varrho_1) - cos\, \sigma_1 (cot\, h_2 cos\, \varrho_2 - sin\, \sigma_2 sin\, \varrho_2)}{cos\, \sigma_2 (cot\, h_1 sin\, \varrho_1 + sin\, \sigma_1 cos\, \varrho_1) - cos\, \sigma_1 (cot\, h_2 sin\, \varrho_2 + sin\, \sigma_2 cos\, \varrho_2)} \quad . \quad (2)$$

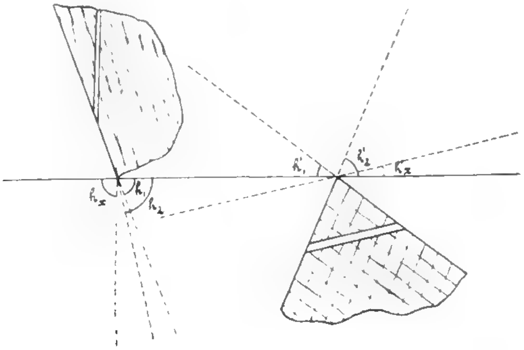

Fig. 1.

With an augite-crystal the planes m_1 $(\bar{1}10)$ and m_2 (110), being fixed to the projection-plane E $(\perp \mathfrak{c};\ c : \mathfrak{c} = 45°\ 18')$ and to the plane $\perp E$, laid through the normal of m_1 are determined by $\mu_1 = 0$, $\mathbf{r}_1 = 29°\ 20'\ 55''$ (m_1) and $\mu_2 = 112°\ 22'\ 34''$, $\mathbf{r}_2 = 29°\ 20'\ 55''$ (m_2) if $m_1 : m_2 = 92°\ 48'$. In fig. 1 the left section answers to the secant-plane S_1 $(\varrho_1 = 36°\ 30',\ \sigma_1 = 47°)$, the right one to S_2 $(\varrho_2 = 220°\ 30',\ \sigma_2 = 79°)$; the traces of the planes m_1, m_2 and of the twinning-plane x of the interpolated lamel make in these sections with the secant-line $S : E$ the angles $h_1 = -70°\ 34'$; $h_2 = -78°\ 4'$, $h_x = 89°\ 24'$ and $h'_1 = \quad 37°\ 10'$, $h'_2 = 66°\ 44'$ and $h'_x = 13°\ 30'$. With the help of the values ϱ_1, σ_1, ϱ_2, σ_2, h_x and h'_x one finds from (2) for μ the value $\mu = 56°20'$ and from (1) $r = 45°\ 8'$. The plane P is consequently a (100) which is theoretically determined by $\mu = \frac{\mu_2}{2} = 56°11'17''$ and $r = c : \mathfrak{c} = 45°18'$.

Anatomy. — "*Remarks on the reticular cells of the oblongata in different vertebrates.*" By J. J. L. D. Baron van Hoevell. (Communicated by Prof. L. Bolk.)

(Communicated in the meeting of January 28, 1911).

The reticular cells in several mammals have been examined and described, and about some birds we have minute information from Cajal[1]), while Mesdag[2]) also gives excellent descriptions and illustrations of the large reticular cells in one species of bird (Gallus domesticus).

In the reptiles, however, where the reticular cells are singularly conspicuous and characteristically arranged, these cells have never been described, nor have we any information of importance regarding the amphibians and various species of fishes[3]).

A comparative study of the reticular cells has never been made, although these elements exhibit great differences in the vertebrate stem together with points of resemblance. Even in animals of the same class noticeable differences are found.

It cannot be denied that, as long as so little is known with certainty about the nature and significance of the reticular cells, it would be somewhat rash to make comparisons, since the possibility of dissimilar quantities being compared with each other is not excluded. In my investigations I have confined my attention principally to the largest reticular elements, because these are the most fit for comparison. Still less is known of the small reticular cells than of the largest. A sharply defined boundary of the larger reticular cells from the smaller is, however, not always possible as yet. Besides the large reticular cells, therefore, I have traced the smaller ones also as much as possible, although the chief aim of my research was the arrangement of the larger elements. I have examined series of frontal sections coloured after van Gieson or with carmine.

The animals which I examined were:

one cartilaginous fish: Raja;

one amphibian: Rana;

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[1]) Contribucion al Estudio de los ganglios de la substantia reticular del bulbo. Trabajos del laboratorio de Investigaciones biologicas. Tomo VII fasc. 4°. 1909.

[2]) Bijdrage tot de ontwikkelingsgeschiedenis van de structuur der hersenen bij het kippenembryo. Inaugural Dissertation. Groningen 1909.

[3]) Special mention must be made of the large cell elements of the oblongata in the Cyclostomes, lately described by Tretjakoff Whether the large Mullerian cells of the Cyclostomes are to be classed with the large reticular cells of the bulb of other animals is not certain, but there is much which pleads for a homology (Cf. Tretjakoff: Das Nervensystem von Ammocoetes. II. Gehirn. Archiv. für mikroskopische Anatomie und Entwickelungsgeschichte. Vol. 74, 1909).

two reptiles, Alligator sclerops and Chelone midas;
one bird, Ciconia alba:
and several mammals, viz.:
two Marsupials: Macropus robustus and Didelphys;
two Rodents: Cavia cobaya and Lepus cuniculus:
one Ungulate: Equus caballus
and one cetacean: Phocaena communis.

Raja.

In viewing a series of frontal sections through the oblongata of Raja, one observes everywhere the large reticular cells arranged fairly uniformly along the lateral and ventro-lateral border of the fasciculus longitudinalis posterior. Only in the caudal part of the oblongata, on the level of the extrance of the X^th^ roots, is a different form to be found owing to the reticular cells here being greatly massed in the raphe.

The reticular cells of the bulb of Raja form one continuous series. They are not, however, distributed equally over the bulb; on some levels they are to be found more massed, so that one might speak of reticular nuclei. The reticular cells in Raja can be divided — on descriptive anatomical grounds — into 3 groups, viz.: 1st, a caudal group, occurring on the level of the extrance of the X roots, 2nd, a group occurring on the level of the entrance of the VIII roots, and a 3rd group, which comprises the series of reticular cells frontally from the VIII's entrance. For the sake of convenience these may be termed *nucleus reticularis inferior, medius,* and *superior.*

Fig. 1 represents a more caudal level, Fig. 2 a more frontal level of the X roots. The accumulation of cells between the fasc. longit. post. and the base can be seen, with a marked raphe nucleus (figs. 1 and 2 : *a*.) and wings which stretch out sideways, wreath-like, underneath and along the border of the fasc. long. post. Some of these cells lie fairly dorsally, lateral from the fasc. long. post. (Figs. 1 and 2 : *b*). Other cells lie more ventrally in the formatio reticularis. (Figs. 1 and 2 : *c*). A few smaller reticular cells lie rather far laterally. (Figs. 1 and 2 : *l*). The reticular nucleus of the X region can be defined caudally as well as frontally. In the caudal direction the number of cells gradually decreases both in the raphe and in the formatio reticularis, while the cell-type also grows smaller. Frontally from the entrance of the X roots the number of reticular cells likewise decreases, so that between the X and VIII root-entrances a region occurs, where but few reticular cells are found. On the level of the entrance of the octavus another massing of reticular cells is found (Fig. 3). There 6—8 large cells per section are to be found in each bulbus-half, arranged round the ventro-lateral border of the fasc. long. post; the most dorsal lie almost in the middle of the dorso-ventral diameter of the bulb (Fig. 3 : *b*.), and the others medio-ventrally from there, more towards the lower border of the fasc. longit. post. (Fig. 3 : *c*.) A few smaller cells have a more ventro-lateral position. - In the raphe only a few smaller cells occur.

Frontally from the VIII-entrance the number of large reticular cells again decreases, and 3 - 5 per section are found. (Fig. 4 : *b*. and Fig. 5 *b* and *c*.)

The position is almost the same as on the VIII level. The small, ventro-laterally situated cells are also seen again frontally from the VIII entrance, the most clearly just behind the *V* root entrance. Fig. 4 shows a section through the motor *V* nucleus. Fig. 5 a section frontal from that. With slight variations in the number of the cells the series of reticular cells continues as far as under the frontal boundary of the Bracchia cerebelli and, where the Bracchia disappear from the sections, it is seen only sporadically.[1])

In the raphe merely a few smaller cells occur frontally from the VIII's entrance.

Neither on the VIII level nor frontally from it is there any trace of a raphe nucleus proper.

Rana.

In the *amphibia*, where the arrangement of all the cells remains periependymal, the making of a distinction between reticular cells and other cellular elements is too difficult to allow of details being learned about their topography.

Alligator Sclerops.

The large reticular cells in the oblongata of the alligator can be divided into 2 principal groups. The most caudal group lies on the level of the entrance of the *X* roots and contains a reticular nucleus, capable of being fairly sharply defined. This nucleus commences, caudally in the oblongata, as a little cluster of small reticular cells in the raphe and under the fasc. long. post., while a small group of cells is also to be seen on caudal sections ventro-laterally in the

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1) More frontally in the midbrain again a larger amount of reticular cells occur. This is, however, beyond my scope.

formatio-reticularis, partly polygonal and partly somewhat spindle-shaped. According as one examines frontal sections, more and larger reticular cells will be seen. On the level indicated by Fig. 6 [1]) the reticular nucleus has attained a considerable size. Also the lateral nucleus l_1 is well developed on this level.

Fig. 6. Alligator sclerops.

Fig. 7. Alligator sclerops.

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[1]) In considering the drawing it must be borne in mind that the oblongata of the Alligator is markedly bent and that the direction of the section has been chosen perpendicular to the base on the level of the VII-root, so that the caudal sections are not perfectly perpendicular to the longitudinal axis of the oblongata. In Figs 6, 7, and 8, the dorsal half represents a more caudal level than the ventral half.

Slightly more caudally than is shown by Fig. 6, the hypoglossus-cells (or the anterior-horn cells; a sharper distinction between them cannot be made by my method) take a more ventral position, and can only with difficulty be distinguished from the reticular cells which lie in the lateral border of the fasc. longit. post.

Fig. 7 represents a section which passes through the entering X roots. The same nucleus with large cells as in Fig. 6 is met with here, though on a more frontal level. The large cells can be seen lying partly in the raphe, partly in the formatio-reticularis, spread wreath-like in a ventro-lateral direction, while a small group lies more or less isolated somewhat more ventrally. (Fig. 7*c*.) Laterally in the periphery a nucleus can be seen (Fig. 7 l_2), which I cannot determine with certainty to be the continuation of the lateral nucleus (l_1) of Fig. 6, since nucleus l_1 decreases frontally, so that on a level between Fig. 6 and Fig. 7 very few cells lie there which cannot be distinguished from the remaining scattered cells of the formatio reticularis.

The large reticular cells on the level of the VIII root entrance can be taken together in one and the same group with those occurring more frontally. This group is easily distinguishable from the more caudal reticular nucleus of the vagus region.

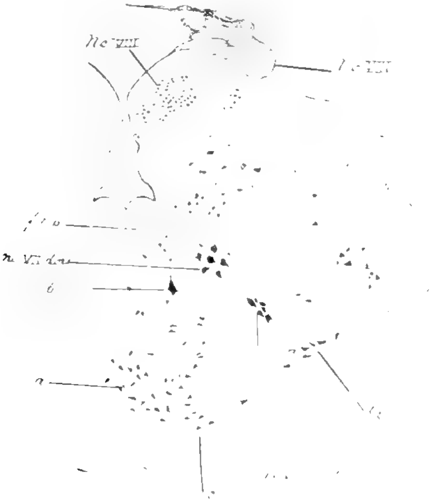

Fig. 8. Alligator sclerops.

Fig. 8 represents a section through that part of the oblongata that may be regarded as the transition or boundary region between vagus and octavus region. On several of the sections only one single large reticular cell is to be seen on this level; in Fig. 8, one can be seen in the border of the fasc. long. post. (*b*). Ventrally in the raphe (*a*) and next to it (*c*), between the fasc. longit. post. and the base, a large number of smaller reticular cells are seen. Situated ventro-laterally on the periphery are a group of polygonal cells (Fig. 8, l_2), which lie dorso-medially in one straight line with two other groups. The most dorsal of the three groups contains motor VII. root-cells, the middle one is very likely a more ventral VII. nucleus. It is highly improbable that the most ventral of the three (l_2) is a VII. nucleus, as has already been pointed out by KAPPERS [1]). This last group forms the continuation of group l_2 of fig. 7. I consider them as reticular cells.

On a level slightly more frontal than is shown by fig. 8, more large reticular cells are again seen. Fig. 9 represents a section passing through the VIII. root-entrance. In the raphe large cells can nowhere be seen in sections taken more frontally than fig. 8, though in fig. 9 a few small cells can be seen in the raphe. By this fact too the reticular nucleus of the vagus region is distinguished from the reticular cells of more frontal regions of the oblongata. The arrangement of the large cells next the lower border of the fasc. longit. post. (*b*) and more ventrally (*c*) medially from the large oliva superior is seen in the figure.

Fig. 9. Alligator sclerops.

I still wish to call attention to some very large polygonal cells occurring in the grey matter of the radix descendens nv. V. and to

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[1]) See also Verhandel. Kon. Acad. v. Wet. 2de Sectie, Part. 16, No. 4. (Map E. and page 64).

the fact that a few of these lie very peripherally or laterally in tha grey matter. Immediately above the point of the oliva superior and lateral from the olive lie some smaller cells.

The series of large reticular cells of the octavus region is continued frontally without interruption. In Fig. 10, which represents a section passing through the caudal part of the motor V. nucleus, the large reticular cells lie as a circumscribed group in the middle of the

Fig. 10. Alligator sclerops.

Fig. 11. Alligator sclerops.

diameter of the bulbus. Laterally from it a dorso-ventrally stretched nucleus is seen which is probably a ventral motor Vth nucleus (KAPPERS)[1].

Fig. 11 represents a section through the entering V root. The large reticular cells have partly kept their position more in the middle of the formatio reticularis, but partly also lie more ventro-laterally, stretching out to the upper side of the frontal rest of the olive, which is seen on this level, as in fig. 10, as a small mass of grey matter (indicated in the figure by dots) with one single little cell. Medially from the frontal rest of the olive, a small group of little polygonal cells occur regarding which I do not venture to say whether they belong to the reticular cells or to the grey substance of the lateral lemniscus (fig. 11*x*).

In the raphe there is a nucleus of small cells, which seems to have no connection with the other cells of the formatio reticularis. (fig. 11, nr. parvoc. sup r.); I should like to give this nucleus the name of *nucleus parvo-cellularis superior raphes* in contrast to the cluster of large raphe-cells, which form part of the reticular nucleus of the vagus region. In Fig. 11, under the angle of the ventriculus quartus a group of cells can be seen which in position agree with the nucleus loci coerulei[2]) beginning more frontally in mammals.

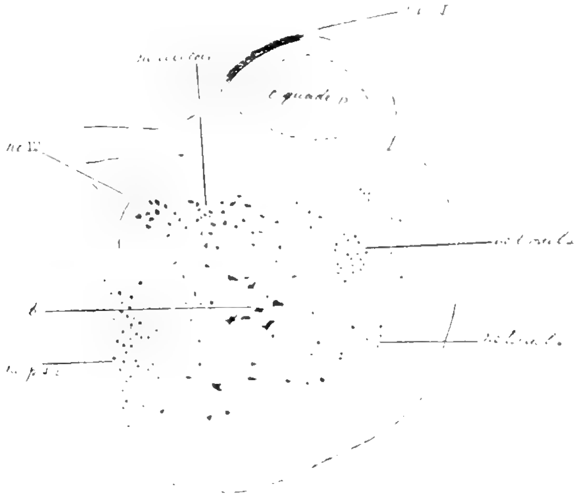

Fig. 12. Alligator sclerops.

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[1]) Especially from a comparison to chelone midas this is probable; in chelone a similar nucleus occurs at this place, which frontally coincides with the motor V-nucleus. See Verhandl. der Kon. Akad. van Wet. 2de Sectie, Part XVI N⁰. 4, pages 39 and 40. Map.E.

[2]) As in the lower mammals this nucleus is not pigmented here.

More frontally from Fig. 11, we again find a less lateral arrangement of the large reticular cells and the number met with per section also diminishes. Fig. 12 represents a section through the praetrigeminal region of the oblongata of the Alligator. The section here shown passes through the posterior pole of the tuberculum quadrigeminum posticum and also intersects the IV nucleus. The arrangement of the large cells, as occurs here, in the middle of the diameter of the bulbus, continues frontally to the end of the series of reticular cells, i. e. to behind the III nucleus, where the large reticular cells are sporadic The raphe nucleus with small cells, which can also be seen in fig. 12, ceases on nearly the same level as where the large reticular cells become sporadic. These raphe-cells maintain a more independent character with regard to the other reticular cells.

Chelone Midas.

Chelone differs in many respects from Alligator. In the caudal part of the oblongata it shows some resemblance to the latter as regards the appearance of the reticular cells. Nor is the praetrigeminal region markedly different from that in Alligator. On the level of the entering VIII and V roots, however, an entirely different aspect is presented. Following the same order as I took in examining the other animals I can state the following details about the reticular elements of Chelone: On the level of entrance of the X roots, one reticular nucleus is found, which resembles the nucleus found in that region in the Alligator in so far as the large reticular cells are arranged in the same way in the raphe and along the lower and side border of the fasc. long. post. In Chelone, however, no reticular cells are spread so far laterally in the formatio reticularis. Also the groups l_1 and l_2 of Alligator (Pl. 6, 7 and 8) are wanting in Chelone. The reticular group of the vagus region is sharply limited orally, owing to the fact that, on the level of the extrance of the VIII, large reticular cells occur only sporadically and but a few smaller reticular cells are present there [1]). On the level of the motor trigeminus nucleus on the other hand, there is a cluster of large reticular cells, not only along the lower and outer border of the fasc. long. post., but also in the raphe, which I did not find on this level in other animals. (See fig. 13).

On the level of the caudal half of the motor V nucleus the large cells are even found principally in the raphe; on the level of the frontal half of this nucleus, however, there are as many lateral in

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[1]) The nc. Deiters is well developed. I found no oliva superior.

Fig. 13. Chelone midas.

the bulb as in the raphe. Orally from the motor V nucleus the large reticular cells lie almost in the middle of the diameter of the bulbus, while in Chelone as in Alligator, a raphe nucleus of small cells also occurs in the frontal part of the oblongata (*nc. parvocell. sup. raphes*) which nowhere shows any connection with the other reticular cells.

Ciconia alba.

I examined only one bird, viz. Ciconia alba, in the study of which a series of frontal sections coloured after VAN GIESON was used.

I found the reticular cells for the most part agreeing with the descriptions, which CAJAL gives of these elements in birds. For the details, therefore, I refer to his description. I wish to touch merely on the following points.

The large reticular cells do not extend in Ciconia so far caudally in the oblongata as they do in the lower animals I have described. If the sections in frontal direction be followed, only smaller reticular cells are first seen along the lower border of the fasc. long. post., and more laterally in the formatio reticularis. Then a few very small cells also appear in the raphe. More frontally the reticular cells become more numerous and include larger cells. The cells in the raphe remain somewhat inferior in size to the more lateral cells in the same section; this relative size continues to the level of the VIII root-entrance, where giant-cells occur also in the raphe. Considering that the transition is gradual, however, the boundary where these giant-cells begin in the raphe cannot be sharply defined.

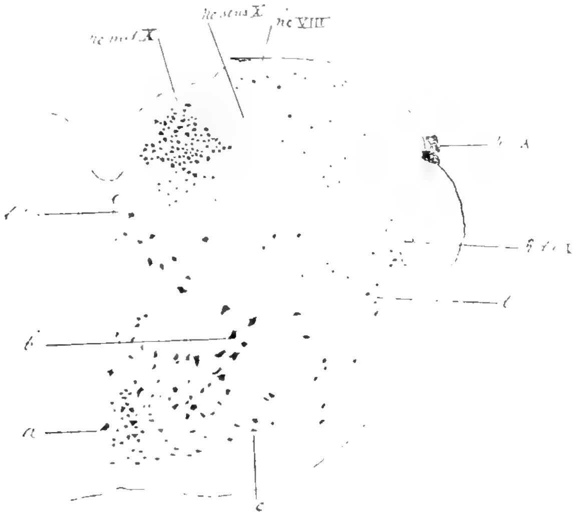

Fig. 14. Ciconia alba

Fig. 14 represents a section passing through the oblongata of Ciconia, slightly frontally of the XII nucleus or through the frontal pole of that nucleus [1]. In this section the connection of the laterally situated giant-cells with the raphe cells which are rather smaller, can be observed.

Cajal describes on the level of the vagus roots only the giant-cells, which lie more laterally in the formatio-reticularis, but neither mentions nor illustrates anything of raphe cells on this level. The large cells lying lateral from the vagus region are collected by him into a separate nucleus and distinguished from the remaining more frontally situated cells by reason of a peculiarity in the course of the axis cylinders [2].

By my method of research I was not able to find any such, or similar, distinction: according to van Gieson preparations the reticu-

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[1] Whether the dorsal group of cells in the border of the fasc. long. post. are still motor XII root-cells, I do not venture to decide.

[2] The cells of his "*nucleo magnocellular inf.*", i. e. the reticular cells lying in the region of the vagus-root, send their axis cylinders for the greater part to the contra-lateral bulbus-half, after decussating dorsally in the raphe, while all the other more frontally situated reticular cells send the axis-cylinders chiefly caudally in the via homolateral (in, or next, the fasc. longit. post.) or caudally and frontally after bifurcation.

lar cell-massing of the vagus region of the oblongata continues unnoticed in that of the octavus region.

In fig. 14 there is visible under the Radix spinalis nervi V a tiny group of small cells (*l*), which form the frontal pole of a circumscribed group of small and medium-sized cells, the meaning of which I cannot conceive.

The cell clusters in the caudal part of the oblongata of Ciconia, which in position agree with the olivae inferiores of mammals, and in the lateral part of which polygonal cells are found connected with the reticular elements, are no longer present in fig. 14.

For the further description of the birds I refer to CAJAL's excellent work. The basal position of a large part of the reticular elements on the VII and V level is particularly striking in his drawings. I found it so in Ciconia also, and will merely mention still that the nc. parvocellul. sup. raphes also occurs in Ciconia.

Mammals.

In the mammals which I examined I found the large reticular cells in the oblongata arranged in a way which principally is the same in all of them. I only found gradual differences and some differences in the relationship of details.

The smaller reticular cells form groups of greater or less size which generally cannot be sharply defined, though where I succeeded in doing so, I received the impression as if the groups of smaller reticular cells also agree in principle with each other in the mammals. In how far the differences which occur are connected with other differences in the formation of the oblongata, I have not been able to decide; to bring out all those details I should have to give a complete series of drawings of each animal, which would lead me too far. I shall therefore content myself with describing two animals in which the peculiarities of the large reticular cells were the clearest, viz. the giant kangaroo (Macropus robustus), the caudal part of which I shall describe, and the horse, of which I shall illustrate the frontal part on account of the peculiarities being the most pronounced there.

The large reticular cells are found in Macropus and in the horse specially massed in two places: one cluster lies in the vagus and octavus region and attains its greatest development at the caudal boundary of the VIII root-entrance, the other lies on the level of the motor V nucleus.

Fig. 15 shows a section passing through a caudal level of the oblongata of Macropus; one of the X roots is visible in the figure.

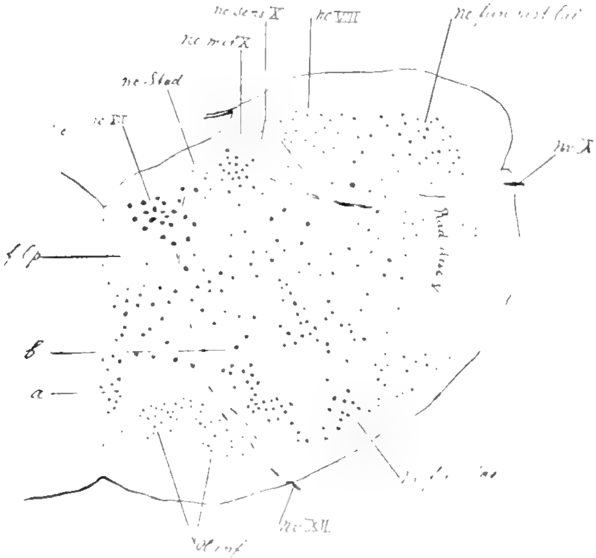

Fig. 15. Macropus.

Fig. 16 represents a section through the caudal boundary of the VIII root-entrance in the same animal.

Fig. 16. Macropus.

On the VIII level distinct giant-cells are to be seen in the raphe as well as more laterally in the formatio reticularis. According as one proceeds more caudally, however, the type of cell becomes smaller, in the raphe rather sooner than in the formatio reticularis.

Fairly far caudally there continues to be a clear connection between the raphe cells and the reticular elements situated more laterally.

In fig. 15 this connection is still visible. The largest reticular cells which occur here are, however, no longer giant-cells.

In fig. 15 a part of the nc. funiculi lateralis can still be seen, which nucleus is well developed in Macropus, and attains its greatest size on a level caudally from fig. 15. In how far there is a connection between the elements of this nucleus and the other reticular cells [1]) I cannot make out. This also applies to the series of cells lying laterally adjacent to the oliva inferior, and there are also doubts about the small group of cells situated ventrally against the radix descendens V as also about the small series of cells medio-dorsal from them, also visible in fig. 15; in this last case because they may for a part contain ventral motor root-cells. In proportion as these small groups of cells (also the nc. funic. lat.) may be classed together with the rest of the reticular cells, a different picture of the spreading and arrangement of these elements will naturally be obtained.

Peculiar in any case is the way in which the reticular cells, arranged, more or less, in rows, are spread from the raphe in a ventro-lateral direction in undulating lines, laterally and ventro-laterally through the formatio reticularis. They form an arch over the oliva inf. and where the nc. facialis appears in the sections (fig. 16) they extend to that nucleus. Where the VII nucleus ends a more lateral spreading can be seen.

As long as so little is known about the nature and the significance of the reticular cells, a rational division into groups is impossible. That the various writers differ in their division and nomenclature of the reticular cells seems to me very comprehensible [2]). In my opinion it is not desirable for the present to make any divisions into groups

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[1]) MARBURG, in his atlas, sometimes calls the nc. funic. lat. also nc. retic lateralis. (See: Microscopisch-topograph. Atlas der menschlichen Zentral Nerven systems).

[2]) The reticular cells lying round the XII roots were taken together by KÖLLIKER as *nc. reticularis diffuses*; he mentioned them "besonders in den lateralen Theilen der formatio reticularis" and medially "bis gegen die Raphe hin."

The cells lying medially from the XII roots are considered by OBERSTEINER as *nc. funiculi anteriores*, and by MISSLAWSKI and VAN BECHTEREW as *nc. respiratorius*.

The large cells occurring on the level of the VIII entrance and caudally from that, have been described by ROLLER, and are termed by most writers *nc. centralis inferior* ROLLER.

which cannot be sharply defined from each other. Even the collection of the giant-cells, of the octavus and of the rather more caudal region into a separate nucleus, although these cells are clearly larger than the largest reticular cells which occur in the vagus-hypoglossus region, seems to me to be undesirable at the present time. The transition in the size of the cells is after all a gradual one, and whether here, as in birds, by reason of a different course of the axis-cylinders, the cells of the vagus region of the oblongata have to be distinguished from those of the octavus region or not must be decided by further histological research.

By my method of research I could not make distinctions based on cell-structure differences between the cells: I must therefore refrain from passing an opinion.[1])

If we collect all the reticular cells of the caudal half of the oblongata — calculated to about the frontal boundary of the VIII root-entrance — into one nucleus, we might term this *nucleus reticularis inferior*, and to indicate that the cells extend to the raphe and partly collect there, we might distinguish a *pars raphes* and a *pars lateralis*; and possibly also include the *nc. reticularis funiculi lateralis.*

On a level slightly frontal from the VIII root-entrance the number of reticular cells decreases, to increase again on the level of the V nucleus. On the level of the motor V nucleus and in more frontal parts of the oblongata I no longer found any giant cells in the raphe except sometimes (Macropus) a very few on the level of the most caudal part of the mot. V nucleus. Cells are indeed found in the raphe which agree with the nc. pontis and still further frontally, immediately behind the corpora quadrigemina, a raphe nucleus of small cells. To these cells, which have probably another origin and meaning, I shall return later.

The large reticular cells in the oblongata of the trigeminal and praetrigeminal regions of the mammals, with the exception of phocaena, showed a peculiarity in their arrangement which was not equally conspicuous in all. The cells are divided more or less clearly into two groups, one of which remains lying more dorsally in the bulb while the other has shifted in a ventro-lateral direction, coming to

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[1]) The large reticular cells which occur in man on the caudal part of the VIII root-entrance, are counted by JACOBSOHN as belonging to two reticular nuclei, which lie partially through each other: his *nc. giganto cellularis formationis reticularis* and his *nc. motorius dissipatus formationis reticularis.* This distinction he makes solely on the ground of cell-structure differences, while he states that the cells of the *nc. mot. dissip. f.r.* are in general smaller than those of the *nc. gig. f.r.*, although they sometimes attain the size of the latter.

lie against the lateral lemniscus. In the horse I found this displacement the plainest: there the reticular cells even lie partly between the fibres of the lateral lemniscus.

In Macropus these two groups are still clearly connected; in other animals, e.g. the rabbit, I found a relationship which is medium between the horse and Macropus.

Figs. 17, 18 and 19 represent sections through the oblongata of the horse. The level of the sections is sufficiently clear in the drawings.

The large reticular cells are seen to be split into two groups. The ventro-lateral group maintains its position against, and in, the border of the lateral lemniscus. Where, on a more frontal level, the lateral lemniscus lies more dorsally in the section, the reticular cells also lie more dorsally in that section (cf. Figs. 18 and 19).

Fig. 17. Equus

In figs. 18 and 19 I have indicated the boundary of the nuclei pontis by a dotted line. In the vicinity of the raphe a bulging of the nuclei pontis into the oblongata can be seen on fig. 18, indicated by the dotted line. In the horse, the cells of this group cannot be sharply defined from the other cells of the nc. pontis. In some animals, however, e.g. the rabbit and especially Phocaena, the cells of this dorsal group are so distinctly different from the other nc. pontis, and send out such peculiar off-shoots in lateral and dorsal

Fig. 18. Equus.

Fig. 19. Equus.

directions that this cell-group has probably a special significance and is worthy of a separate name. The name of nc. *reticularis tegmenti* given to it by v. BECHTEREW is not, in my opinion, a very happy choice, as it might be confused with the other reticular cells in the tegmentum on the same level. I would propose to name this group after him who first described these cells, viz. *nc. reticularis* BECHTEREW, in order to avoid a regional division for the present. Whether the small group of cells in the raphe in fig. 17 belongs to the nc. retic. BECHTEREW, I do not venture to state with certainty. They are separated caudally from the pars raphes nuclei reticularis inferiores, but frontally are connected with the nc. pontis and the nc. retic. BECHTEREW. Their dorsal position in the raphe renders a connection with the nc. BECHTEREW more reasonable, while the extension caudally from the pons makes it not probable that they belong to the nuclei pontis[1]).

Frontally from the nc. retic. BECHTEREW there is a nucleus of small cells (fig. 19) which ought probably to be distinguished from the other reticular cells, and is very possibly homologous to the nc. parvoc. sup. raphes of the reptiles, at least to the frontal part of this nucleus. VON BECHTEREW described this first in man as *nc. centralis superior;* later he renamed it *nc. centralis superior medialis s. internus*, or simply *nc. medialis* to distinguish it from the large cells occurring laterally in the formatio reticularis, which he calls *nc. centralis sup. lateralis.*

Let us now return to the large reticular cells. Frontally from Fig. 19 we see the large reticular elements soon take up a more circumscribed position, almost in the middle of the bulbus-half, owing to the disappearance of the ventro-lateral cells from the sections. Somewhat farther frontally still we see that the more dorsal large reticular cells also become fewer.

The whole series of these large elements of the trigeminal and praetrigeminal region of the oblongata I would collect under one name, viz: *nucleus reticularis superior*, which may consist further of a *nc. superior centralis s. dorsalis* (*b.*) and a *nc. superior ventrolateralis* (*b.*[1]).

This nc. sup. dorsalis s. centralis thus coincides with the nc. centralis sup. lat. (BECHTEREW), while similar to my nc. sup ventro-lateralis would be the nc. tegmenti lat. described by KÖLLIKER in man as occurring between the Lemniscus lat. and the Bracchia anteriora[2])

Herewith I conclude the description of the arrangement in Macropus and Equus which on an average is the same in other mammals. The relations found in cavia, rabbit, cat, and man were in principle little different from those mentioned above.

Only in Phocaena I found a more primitive arrangement, as I did

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[1]) In a deaf born cat, the nucl. ret. Becht seemed to be reduced.

[2]) I suppose that the *nucl. paralemniscalis inferior* (cells situated medial against the Lemn. lat) described by KOHNSTAMM in the rabbit, partially agree with my nc. sup. ventro-lateralis. (Journal f. Psychologie u. Neurologie **1910**).

not find here a splitting of the nucleus reticularis superior into a dorsal and ventro-lateral group respectively (b and b_1 resp.). The cells are here spread more equally through the formatio reticularis, principally more dorsal in the bulb. Whether of the cells lying between the bundles of the lateral lemniscus some must be considered as very ventrally situated reticular cells, belonging to the said nc. reticularis, I do not venture to decide. I do not consider it probable, however.

Owing to the extreme diffuseness in the arrangement of the reticular elements of the various vertebrates and the frequent difficulties in defining these from non-reticular elements, it is not easy to state the result of my labours in a few words. Nevertheless I believe I may place in the foreground the following facts.

1. As far as I know, in the lateral field of the oblongata, a more or less pronounced massing of the large reticular cells occurs in all vertebrates except in cyclostomes and amphibians.

2. In all animals, moreover, large cells occur in the raphe in the *caudal part* of the oblongata; in the frontal part of the oblongata the large cells are wanting in the raphe, with the exception of chelone, where they also occur on the level of the trigeminus-nucleus as an independent group, distinct from the vagus group.

3. In the reptiles, birds and mammals a raphe-nucleus consisting of *small cells* is constantly found in the anterior part of the oblongata about the posterior boundary of the corpora quadrigemina posteriora.

4. The frontal group of the lateral reticular cells undergoes in the phylogenesis a strong increase, and a division in such a way that a portion of these cells retains their dorsal position, while another portion (the number varies in the different animals) acquires a more ventro-lateral position on the lateral lemniscus, or directly medially to it.

5. Phocaena exhibits a deviation from the general mammalian type by a lesser differentiation of the reticular nuclei in the anterior part of the oblongata.

Microbiology. — "*Pigments as products of oxidation by bacterial action.*" By Prof. M. W. Beijerinck.

(Communicated in the meeting of February 25, 1910).

The following experiments make it possible easily to find some notable bacteria more or less common in our surroundings and partly not observed hitherto.

1. *Formation of Protocatechetic acid from Chinic acid.*

As Löw[1]) had shown that 1 proc. solutions of calcium chinate become brown when exposed to the air by the formation of protocatechetic acid, Emmerling and Abderhalden[2]) have investigated this biochemism bacteriologically. They neutralised 10 proc. solutions of chinic acid with calcium carbonate, added 0.5 proc. peptone, 0.1 proc. kalium phosphate, and 0.1 proc. magnesium phosphate, inoculated this mixture with a few drops of an infusion of putrefying meat, and cultivated for some weeks at 35° C. They obtained protocatechetic acid together with a slimy bacterial mass in the liquid, from which it was possible to isolate a likewise slimy *Micrococcus*, which proved to be the cause of the production of the latter acid and was named *M. chinicus*.

The reaction goes after the formula:

$$\underset{\text{Chinic acid}}{C_7H_{12}O_6} + O = \underset{\text{Protocatechetic acid}}{C_7H_6O_4} + 3H_2O$$

whereby at most 12 proc. chinic acid is converted; into what the remaining 88 proc. change is not noted by these experimenters. It is remarkable that only one atom of oxygen takes part in this reaction.

As the said authors had not applied in their experiments the so intense colouring of ferrisalts by protocatechetic acid, it seemed desirable to make use of it for the easier recognition of the inferred bacteria.

To this end the experiment was effected as follows:

For the rough or preliminary cultivation a liquid was used of the composition:

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[1]) Berichte der Deutschen Chem. Gesellschaft, Bd. 14, pag. 450, 1902.

[2]) Ueber einen Chinasäure in Protocatechusäure überführenden Pilz. Centralblatt für Bakteriol. 2te Abt. Bd. 10, Pag. 337, 1903.

Tapwater	100.00
Dikaliumphosphate	0.05
Ammoniumchlorid	0.05
Calciumchinate $(C_7H_{11}O_6)_2Ca + 10H_2O$	0.1 to 10
Ferrichlorid	0.01

In a wide ERLENMEYER flask, so that a strong aëration occurs in the thin layer, inoculated with soil and cultivated at 20° to 25° or 30° to 35° C., the liquid colours deep black after a few days, in consequence of the formation of ferriprotocatechate.

To purify the bacterial culture a trace is transferred to a similar medium and cultivated at 20° or 30° C.

If this culture is sown on a medium of the same composition but solidified with agar and containing some ferricitrate[1]), colonies are obtained, from the cultures kept at 20° to 25° C., of different varieties of *B. fluorescens*, and from those kept at 30° to 35° C. chiefly of a *Micrococcus*, all lying amid diffusion fields of ferriprotocatechate of an intense violet or red colour. This *Micrococcus* belongs perhaps to the same species as that described by EMMERLING and ABDERHALDEN, but then certainly to another variety, for it does not produce slime, neither in presence of peptone nor of ammonium-salt. This form, very common in our environment and which can be obtained with various other organic salts in a similar way as with chinate, I shall name *Micrococcus calco-aceticus*, as calcium acetate is very fit for its accumulation. Here it may be observed that acetates are also very useful for the accumulation of certain varieties of *B. fluorescens non-liquefaciens* which still grow at 30°C.

Streaks of these various bacteria on broth agar with one proc. calcium chinate, and a little ferricitrate, or on the above medium, give again deep black or red-coloured diffusion fields of ferriprotocatechate.

Part of the chinate oxidises directly to water and calciumcarbonate which precipitates as crystals dyed deeply violet, by having sucked up the ferrisalt of the protocatechetic acid during their crystallisation.

Other species, able to convert the chinic acid into water and calciumcarbonate or protocatechetic acid, but not found in the foregoing experiments, are mentioned in the following table where it is indicated by + and — whether the substances placed at the head are either or not formed. These experiments were made with broth agarplates with 1 proc. calciumchinate at 30° C., or use was made

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[1]) Ferricitrate does not give a precipitate of ferriphosphate in the somewhat alkaline broth.

of the above named nutrient liquid containing ammonium chlorid, after its solidification with agar.

From chinates result by	Protocatechetic acid	Calcium-carbonate as crystals	Remarks
Bacillus prodigiosus	+		
" *punctatus*	—	—	
Aërobacter coli	—	—	
" *aërogenes*	+	—	Some varieties
" *liquefaciens*	—	—	
Pseudomonas aromatica	—	—	
" *fluorescens non liquefaciens*	+	+	Some varieties
" *fluorescens liquefaciens*	+	+	Some varieties
" *pyocyaneus*	+	+	
Proteus vulgaris	—	—	
Microspira tyrosinatica	—	—	
Micrococcus calco-aceticus	+	+	All varieties
Acetic acid bacteria	—		
Yeast species	—		

This table shows that the common species which oxidise chinate to protocatechetic acid, namely the fluorescents, also embrace varieties devoid of this faculty.

The second column is but of relative value, for a number of bacteria oxidise the chinate and grow from it with great intensity without crystallisation of the thereby formed calciumcarbonate. The chinates, belong (with the malates) to the most easily assimilable organic salts for non-sporulating bacteria in general.

It is remarkable that there do not seem to exist spore-forming bacteria which produce protocatechetic acid, for I did not succeed in obtaining microbes from pasteurised materials, such as garden soil or canal mud, which, in solutions or on plates of the before given composition gave rise to an obvious change of colour. But by various spore-formers calciumchinate was changed into carbonate, though slowly.

With exclusion of air solutions of chinate are apt to come into fermentation, as was already observed by Löw, whereby carbonic acid, acetic acid and propionic acid are formed. Hydrogen was not found; the inferred microbes belong to *Aërobacter aërogenes* and allied forms.

2. *Oxidation of Quercite to Pyrogallic acid by Pseudomonas aromatica.*

The knowledge that chinic acid derived from the hexamethylene ring (hexahydrotetraoxybenzoic acid) can so readily be converted by many microbes into an aromatic substance, easily demonstrated by the ferri-reaction, suggested the question if substances exist, related to chinic acid, that behave similarly.

This consideration induced to subject quercite to an investigation analogous to the foregoing, the structure of this substance being the hexamethylene ring, in which 5 atoms of hydrogen have been replaced by hydroxyl. It was proved that also here, under the influence of life, an aromatic substance is easily produced, but at the same time that addition of a ferrisalt to indicate that substance is superfluous; further, that but one single species of microbes seems to exist, of which only some varieties possess the faculty to form that substance.

A more precise investigation showed that here the chemical reaction proceeds quite correspondingly with the oxidation of chinic acid, but that the product is, after all probability, pyrogallic acid, evidently resulting thus:

$$\underset{\text{Quercite}}{C_6H_{12}O_5} + O = \underset{\text{Pyrogallol}}{C_6H_6O_3} + 3\,H_2O$$

Here, too, only one atom of oxygen per molecule of quercite is used. It should be noticed that in these experiments a large portion of the quercite vanishes in another way, probably as carbonic acid and water.

The microbes causing this conversion are very generally distributed in our surroundings, but although there occur among them a number of clearly distinct varieties, they all belong to one and the same species, namely that of the "aroma bacteria", well known in milk and milk products and for the first time distinctly described by MIGULA [1]) as *Pseudomonas aromatica*. It is a polarmonociliate short rodlet, little motile in plate cultures, more so in broth.

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[1]) System der Bakterien, Bd. 2, p. 880, 1900; with fig. Bd. 1, Tab. 1, fig. 8. This description is based on *Bacillus crassus aromaticus* TATAROFF. — Probable synonyms: *B. aromaticus lactis* GRIMMER, Centralbl. f. Bacteriol. 2te Abt., Bd. 8,

The very dark colour of the pigment in an aerated alkaline medium makes it easy to detect the quercite bacterium. If for example, on a broth agar plate with 0.5 proc. quercite, some drops of sewage water are spread, there is much chance that after one or two days at 30° C. some colonies appear that are jet-black, or lie amid a black diffusion field, distributed among the numerous non-pigment producing colonies, which latter are little troublesome, excepting *B. fluorescens liquefaciens*, whose secretion is injurious to the quercite bacteria.

In a previous paper I alluded to a simple experiment whereby aromatic milk results [1]).

To this end milk should be kept at a relatively low temperature, for example at 15° to 20° C., with full admission of air, so that it is left to spontaneous corruption by the aerobic germs it contains. The acidification is at first feeble on account of the low temperature, but it is then that the "aroma bacteria" increase very much and produce the characteristic ester which has not yet been nearer examined.

If of such aromatic milk streaks are made on a quercite plate of the above composition a large number of brown colonies of quercite bacteria appear after 2 × 24 hours at 30° C. An examination of their faculty of producing the aroma in milk proves that it does exist but only in a slight degree. The real "aroma bacteria", which develop by the side of the "quercite colonies" and correspond with these in all other respects, do not possess the power of producing pyrogallol from quercite, hence, though belonging to the same species, they represent other varieties. The quercite bacterium might thus be named *P. aromatica* var. *quercito-pyrogallica*. That *P. aromatica* is so easily distinguished as a species, makes it in this case possible to indicate a character by means of which forms found in nature and seemingly alike, may be recognised as belonging to different varieties. The oxidation function here, thus proves to be very variable, being present or

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S. 584, 1902. — *B. butyri aromafaciens* KEITH, *Bacillus N⁰. 41* CONN; *Pseudomonas fragariae* GRUBER, Centralbl. f. Bact. 2te Abt. Bd. 9, p. 705, 1902. — *Ps. fragariae* GRUBER, Id. Bd. 14, p. 122, 1905, — and *Ps. fragaroidea* HARALD HUSS. Id. Bd. 19, p. 661, 1907. — Perhaps likewise the yellow-coloured *Ps. trifolii* of HARALD HUSS, Id, Bd. 19, p. 68 and 149, 1907, and several other different forms less easily recognisable in the literature are synonyms. — *Bacillus esterificans* MAASSEN, Arbeiten des Kais. Gesundheitamtes. Bd. 15, 1899, is quite another species, producing spores and belonging to the hay bacilli, and thus related with *Granulobacter polymyxa* PRAZMOWSKI.

[1]) Fermentation lactique dans le lait. Archives Neérlandaises, Sér. II. T. 13. p. 350, 1907.

lacking in closely allied forms which are themselves constant and differ only in this quality.

Another character by which the natural varieties of *P. aromatica* are mutually distinct, consists in their very unequal power of liquefying gelatin, this power being intense in some and quite absent in other varieties, with all intermediate degrees. The same is to be observed in the quercite bacteria; hence the variability of this property is in some degree a property of the whole group.

All varieties, apparently without exception, produce in glucose bouillon about 3 cm.^{3} N acid per 100 cm.^{3} liquid. For growth, oxidation and acid formation, peptones are wanted as source of nitrogen, ammonium salts and nitrates can hardly serve as such and only in pure cultures, but by no means in free competition with other microbes.

Although aromatic milk contains a great many quercite bacteria, its flora chiefly consists of other varieties of *P. aromatica*, but the following experiment, based on the principle: slow rising of the concentration of a good nutrient medium apt to produce a slight acidification, makes it possible almost exclusively to obtain the quercite bacteria.

Large glass beakers are filled with 1 L. of distilled water and therein are floated a few small dialysators of parchment paper, manufactured by SCHLEICHER and SCHÜLL, of the shape of experiment tubes, each filled with about 15 cm.^{3} of extract of greenmalt. This extract is prepared by rubbing two parts of greenmalt with three parts of water in a mortar and filtrating after some hours', digeration at room temperature. The clear solution contains relatively little maltose and is of course extremely fit for bacterial growth, where, likewise as in milk, lactic acid ferments are able to develop, but only little lactic acid can be formed on account of the low rate of sugar. Kept in a room where the temperature varied from 15° to 20° C. the spontaneously corrupted infusions in the beakers produced at repeated experiments, made in December 1910 and January 1911, so great an excess of quercite bacteria, that other species could hardly be found in the black mass, obtained by streak inoculations on broth-agar quercite plates.

If instead of submitting the malt extract to dialysis, different quantities of the extract itself were directly added to the water, then, with for the rest like conditions, much less quercite bacteria developed.

The aroma formed in the malt extract is of the same nature as that found in aromatic milk.

Other bacteria but the above named, producing a pigment from quercite, have not been found, neither by experiments with non-sporulating forms at higher temperatures nor among the microbes that remain alive in pasteurised materials.

Finally it may be remarked that quercite (which is not susceptible of alcohol fermentation) is attacked, when no air is admitted, by fermentation bacteria of the *Aërobacter*-group, such as *A. aërogenes*, under production of carbonic acid, hydrogen, and of organic acids which have not yet been more exactly examined.

3. *Oxidation of Tyrosine to Melanine by Microspira tyrosinatica.*

It is well known that the enzyme tyrosinase is able to oxidise tyrosine to a jet-black substance, which is formed at the air from dioxyphenyl acetic acid or homogentisinic acid. It is accepted that this substance originates after the formula [1].

$$\underset{\text{Tyrosine}}{C_9 H_{11} N O_3} + O_3 = \underset{\text{Homogentisinic acid}}{C_8 H_8 O_4} + N H_3 + C O_2.$$

In the experiments now to be treated I could not find ammonia which, according to the formula should come free, probably because all the nitrogen present in the tyrosine, is used for the growth of the bacteria.

Hitherto this conversion had only been studied as a consequence of the action of an enzyme occurring in higher plants and also in higher Fungi. Nobody, however, had as yet described tyrosinase-producing bacteria, whose existence will be referred to in the next lines. As they are rather easily cultivated and are able to produce great quantities of the black pigment formed from tyrosine, which is identic with or closely allied to the melanines of the human body, they are of importance for experimental physiology.

Tyrosine microbes are small vibrios, chiefly occurring in the sea and during the winter months present in the plankton. Fresh water is not however quite devoid of them and without much trouble they may be isolated from sewage water. The forms living in the sea produce, at least as regards the stronger varieties, besides tyrosinase, also tyrosine, and as this takes place from peptone they are to be recognised by the black stains which their colonies produce on broth-agar plates, which, as we have to deal here with inhabitants of the sea, should contain 3 proc. common salt. It is remarkable

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[1] Abderhalden, Physiolog. Chemie. 2te Aufl. p. 367, 1909.

that these tyrosine-vibrios of the sea can be accumulated in seawater with addition of agar as sole source of carbon, ammonium chlorid as nitrogen food, and kalium phosphate. In this respect they show analogy to the gelase vibrios, which secrete the enzyme gelase by which agar is changed into sugar and which are also easily produced in this manner.

Accumulation of these microbes in seawater with tyrosine as source of carbon has not succeeded, as little as with their relatives from fresh water, by corresponding experiments. Endeavours to accumulate the latter from sewage water with tyrosine as source of carbon and nitrogen have produced fluorescents, which thus prove the stronger in the competition at such an "elective" cultivation.

The fresh-water form is fairly common in the sewage water of Delft; to obtain it in pure culture the undilute sewage water must be poured over a plate of the composition:

Tapwater	100
Tyrosine.	0.1
Natrium carbonate	0.1
Dikalium phoshate	0.05
Agar	2

The superfluous water is allowed to flow off the plate, which is cultivated for some days at 30° C.

It is true that here the tyrosine is at the same time source of carbon and of nitrogen, but the method is now a "separative" one, as competition is excluded.

On the second or third day peculiar black spots are seen to appear around some colonies and slowly extend over a distance of some millimeters[1]). The black pigment proves able to diffuse only to a rather short distance, whilst the enzyme itself remains bound up with the bacterial bodies as belonging to the endo-enzymes. That here we have indeed to deal with a true enzyme, is more easily shown in the species of the sea than in the fresh-water microbes. To this end some material cultivated on broth agar is killed by the vapour of chloroform, then transported to a culture plate of the above composition, or to a nutrient liquid of the same preparation, but with omission of the agar. At a temperature of 40° C. the black-colouring is then rather quickly perceived but, of course, without development

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[1]) As the so generally distributed fluorescent bacteria likewise attack tyrosine under production of a light red-brown pigment, there are always found spots of that colour on such culture plates, which can, however, by no means be mistaken for those of tyrosinase.

of the germs. As endo-enzymes may be considered as constituents of the protoplasm, it is not surprising that the reactions with such preparations, containing only dead material, are feeble, for the enzyme itself is for the greater part annihilated. Hence, in my opinion, endo-enzymes are best studied when still within the living cells themselves and by considering them as an essential part of the living protoplasm. Taken in this sense tyrosinase may be called a "respiration enzyme", and it is remarkable that as a product of respiration, beside the carbonic acid, ammonia is formed, instead of water as in the ordinary respiration.

In sewage water only a small number of tyrosine bacteria are found per cM^3. This number may be a little increased by leaving the sewage water for some time at room temperature, then making on plates streaks of the microbes accumulated in the layer at the surface. This microbe layer, very rich in infusoria and flagellates, produces, in particular as it seems in late summer, many more tyrosine bacteria than the sewage water itself. Nevertheless, as said above, it has not been possible to find a really good accumulation method of these tyrosine bacteria, although many trials have been made.

The black pigment can be prepared in great quantities by cultivating the pure microbes at 30° C. in large ERLENMEYER flasks of the said feebly alkaline solution of natriumtyrosinate with the required anorganic salts. The conversion is relatively slow, so that it is complete only after some weeks, but then a liquid is obtained which may be used as ink. Traces of ferrisalts favour somewhat the formation of melanine.

The tyrosine bacteria belong to the genus *Microspira* created by MIGULA. They are very small polar-monociliate, curved rodlets, somewhat varying in thickness, mostly thinner than the cholera vibrios, which for the rest they resemble very much. Like these they quickly liquefy broth gelatin and form on broth agar white, vigorously growing soft masses. Sometimes they are united in long chains; the longest individuals show distinct curves and remind of spirilli. If tyrosine is present in the nutrient medium, many individuals take partly a black colour, swelling up very much and sometimes becoming quite spherical, but the cilia do not become visible. They produce indol, but do not give the nitrosoindol reaction. They grow well in peptone solutions.

The fresh-water form colours broth agar without tyrosine not or only very late, but if tyrosine is added the brothagar grows rapidly black. The black-colouring begins still earlier on the before mentioned culture medium, containing only tyrosine, although the growth on it is much slower than on brothagar.

As nobody had ever before observed tyrosinase formation by bacteria, there is reason to consider these microbes as new for science; the species occurring in sewage water may be called *Microspira tyrosinatica*[1]. It is an organism highly sensible to the nature of the nutrient substances, apt to lose the tyrosinase function by various not yet explained influences, but notwithstanding continuing for years in the laboratory as an hereditary constant species.

§ 4. *The brown pigment formed by the acetic bacterium Acetobacter melanogenum.*

When beer is left to corrupt at the air a film forms at the surface in which *Saccharomyces Mycoderma* and acetic bacteria develop, or only the latter, in accordance with the temperature and other culture conditions. If the corruption takes place at room temperature it will be perceived, when the beer is contained in beakerglasses, that after the film has closed over the surface, some of the beakers slowly assume a dark brown colour and after two or three weeks get so dark, that the beer seems coloured by caramel.

For the isolation of the here active organisms streaks are to be made of the film on wort- or beer gelatin. Then these culture plates being kept *two or three weeks* at room temperature, they show deep brown spots evidently coloured by the same substance which originated in the beer itself, spots in whose centre the colony of a vinegar bacterium is lying. As a matter of course the plates are further covered with colonies of *Saccharomyces Mycoderma* and of ordinary vinegar bacteria.

Culture plates of 100 water, 10 gelatin, 2 peptone, 3 glucose, are also very good for growth and pigment production. The "brown" vinegar bacterium obtained in this way, I recently described under the name of *Acetobacter melanogenum*[2]. It is commonly but not always, a motionless organism, which can only develop on peptone as source of nitrogen and produces the pigment from this substance, if at the same time glucose or maltose is present. Other nitrogen sources but peptone have not been found. The sugar is during the

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[1] Migula's *Microspira nigricans*, System d. Bakteriën, Bd. II, p. 1013, does not liquefy gelatin, but colours it brownish black. Whether tyrosine and tyrosinase occur in this case has not been examined.

[2] Pigmentbildung bei Essigbakterien. Centralblatt f. Bakteriol. 2te Abt. Bd. 29. S. 169, 1911.

growth partly converted into a strong acid, probably gluconic acid. In presence of alcohol much acetic acid is formed. Consequently beer acidifies with great intensity.

Solutions of 10 proc. glucose and 2 proc. peptone in tapwater with 10 proc. calcium carbonate at 25° or 30° C. grow black after a few weeks, the carbonate changing at the same time into calcium-gluconate.

Although for the formation of the pigment the simultaneous presence of sugar and peptone is required, there is cause to admit that the pigment is an aromatic substance, taking rise from peptone alone, whereas this reaction only occurs during the growth of the microbe, for which growth also sugar is wanted. In an earlier paper I gave to such processes the name of auxobolisms.

By the formation of the pigment in the gelatin plates the gelatin not only becomes deep brown, but at the same time quite insoluble in boiling water, which is the more remarkable as the newly isolated stocks of *A. melanogenum* liquefy the gelatin in the beginning (probably by the intense acid production and not by a specific enzyme). Older stocks lose this liquefying power, probably as they become slower in producing acid; their pigment formation, however, remains the same.

Only very few substances render gelatin insoluble in boiling water as for example, formalin and chinon, whilst among the microbes, as far as known, only *Actinomyces chromogenes* (*Streptothrix chromogena*) has the same effect on gelatin by chinon production from peptone. As, moreover, the brown-coloured gelatin reduces silver in an ammoniacal solution of silver nitrate, and produces metallic mercury from an alkaline mercury solution, there is reason to admit that *A. melanogenum* does really produce chinon, this substance giving the same reactions. However the most characteristic reactions of chinon could not be obtained, namely, the blue-colouring of guajac emulsion and the production of iodium from hydroiodic acid. But the secretion product of the brown vinegar bacteria gives quite well the black-colouring with ferrisalts, also characteristic for chinon.

Summary.

The oxidation of chinic acid to protocatechetic acid is brought about by number of microbes belonging to very different groups and is easily demonstrated with ferrisalts. In particular *Micrococcus calco-aceticus* and some varieties of *B. fluorescens non liquefaciens* possess this faculty in a high degree and hence can be found and isolated from mixtures of bacteria.

The oxidation of quercite to pyrogallol is caused only by certain varieties of *Pseudomonas aromatica*, so that we have here a very specialised function. Green-malt extract allowed to grow "aromatic" by spontaneous corruption at low temperature abounds in that species and always contains numerous quercite bacteria which besides, are fairly common in sewage and even in canal water as also in "aromatic milk".

Melanine formation from tyrosine is proper to certain sea-vibrios and to *Microspira tyrosinatica* not uncommon in sewage water and easily found by this reaction. It is a microbe closely allied to the cholera and the photogenic vibrios. The tyrosinase function is sometimes suddenly lost by unknown influences, but may return in the same stock. Notwithstanding, the species can be considered as fairly constant and remains so for years in the laboratory.

Beer, poor in extract, colours dark brown when corrupting at the air. This is owing to the presence of a vinegar bacterium, *Acetobacter melanogenum*, which produces a pigment reminding of caramel from peptone. By the secretion products of *A. melanogenum* gelatin is as it were tanned and becomes insoluble in boiling water. Perhaps chinon is inferred in this process.

In natural varieties of the species of microbes, which in all other respects show no difference, the oxidation function in regard to certain substances may be either or not present, but if present it may be very constant in these varieties.

Zoology. "*The Eutherian and the Metatherian early blastocyst*".
By Prof. A. A. W. Hubrecht.

The careful description of the early development of the Marsupialia by Prof. J. P. Hill in vol. 56, pt., of the Q. J. of micr. Sc., has been anxiously awaited by numerous vertebrate embryologists, who, being acquainted with Hill's important contributions (together with Wilson) to the ontogeny of Monotremes, expected that a firm basis would henceforth be established on which the mutual relationships of the more primitive and the more specialised Mammalia might be built up. In this respect however the valuable publication, above referred to, is a deception. Far from being exhaustive it presents the limited number of observations available in the light of an interpretation in which the distinction of what is normal from what is abnormal, is largely dependent on numerical relations and in which the representatives of the so-called abnormal blastocysts are not fully introduced to the reader, nor sufficiently described at length, to enable the interested student to form an opinion for himself.

And yet this would have been doubly desirable because of the fact that Prof. HILL, who, in his earlier paper on the placentation of Perameles, has so markedly drawn together the Eutheria and the Metatheria, finds in the development of Dasyurus grounds for again separating the two subclasses more definitely.

Immediately after having become acquainted with HILL's first mentioned paper I felt it my duty to attempt to convince myself personally that the differences, just alluded to, do exist and I found in Prof. HILL's laboratory the most hospitable reception and at his hands the most liberal treatment, which permitted me to see and weigh everything for myself, and even to draw and to model such preparations as might seem to favour interpretations different from his own. I cannot too highly value this disinterestedness, thanks to which the problems involved will all the sooner be brought into a light full enough for fellow-workers to draw their own conclusions.

And so I will here attempt to give a brief survey of the principal differences which HILL has detected between the results obtained by him for Dasyurus and my own generalisations, which were chiefly based on personal acquaintance with the Eutherian ontogeny.

There is no doubt that the cleavage phenomena in Dasyurus, up to the 16 cell-stage, are decidedly peculiar and that the arrangement of the 16 cells in two rows of 8 cells each, fully deserves the attention which HILL has directed to it. The first three cleavages seem to occur constantly in a meridional sense. Only the fourth cleavage takes place in a plane perpendicular to the three preceding ones: the result being an aequatorial band of two cellular belts, one composed of 8 smaller cells (representing what HILL calls the formative half of the blastocyst), one other of 8 somewhat bigger cells (the non formative half).

HILL is no doubt justified in emphasizing the points of difference between this stage and the Eutherian morula. They are the following:

a. The Dasyurus blastulastage is normally open above and below, until (very soon after) both the upper and lower solution of continuity will have ceased to exist, thanks to continued proliferation (in the direction of the opposite poles) of the cells constituting the two belts just mentioned.

b. The unilaminar blastocyst does *not* contain an embryonic knob, which has been described by all authors writing on the Eutherian blastotocyst, as a group of cells applied at one spot against the exterior trophoblast, and which is composed of the cells *that will furnish the embryonic* (formative) *ectoderm as well as the whole of the embryonic entoderm*.

In Dasyurus, as HILL repeatedly says, what is by him called the formative hemisphere (itself a derivative of the belt of 8 smaller cells) of the hollow blastocyst, fulfils the part that was just indicated for the Eutheria by italics, whereas the lower or non formative hemisphere of the blastocyst constitutes the trophoblast of the Metatheria, comparable to that of the Sauropsida and Prototheria and *a fortiori* also of the Eutheria [1]).

My own interpretation of the Metatherian morula, given on p. 7 of my article in vol. 53 of the Q. Journ. and not based on any personal observations, has taken its starting-point from SELENKA's figures of early Opossum blastocysts, about which HILL expresses grave doubts and which he refuses to look upon as normal. So here the two specialists who have explained to us the early developmental phases of Marsupials are diametrically opposed, one (SELENKA) describing and figuring the presence — inside of the unilaminar blastocyst — of a mothercell (Urentodermzelle) of the entoderm, whereas the other (HILL) is convinced that normally there is no cellular enclosure inside this unilaminar blastocyst wall of Dasyurus and thus no mothercell of any embryonic knob comparable to the "inner cell mass" of Eutheria in the Marsupials.

For myself I have based my comparative considerations on SELENKA's data, but have interpreted them differently, looking upon SELENKA's "Urentodermzelle" as the mothercell not of the entoderm only, but of the whole inner cell mass (embryonic knob).

The fact that Prof. HILL *does* figure one case (l. c. Pl. 3 Fig. 37) in which a Dasyurus blastocyst contained one big cell in its cavity and that therefore this case — emphatically stated to be *abnormal* by HILL — *does* present a certain amount of comparability with SELENKA's figures above alluded to, made me all the more anxious

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[1]) There is a misunderstanding on p. 107 of HILL's latest paper as to my *not* considering the extra-embryonal ectoderm of Sauropsida as trophoblast. This misunderstanding may have arisen in consequence of HILL having cited the condensed text of my Boston address, while my original paper (Q. J. vol. 53 p. 20, 24, 25) would have left no doubts in his mind and would at the same time have convinced him that the wonderful phenomenon in Dasyurus so excellently figured in his fig. 42—46, 48—50, has been welcomed by me as a beautiful confirmation of my contention that in Sauropsida and Ornithodelphia we ought to identify the so called extra-embryonal ectoderm with the entire trophoblast of Eutheria. Here again the Rauber-cells of the rabbit, of Sorex among others have led HILL astray, as they have formerly done BONNET, and *the intercalation* of embryonal ectoderm into the trophoblastic outer layer has not been sufficiently kept in view, although I have particularly called attention to its details in Tupaja, Tarsius, Sus, Cervus and so many others.

to become personally acquainted with his early blastocysts of Dasyurus among which, as he distinctly mentions, in addition to the one figured in fig. 37 he has come across yet *more* "abnormals." Three of these "abnormals" are here figured and are seen to contain proliferating cells. Their aspect in many respects resembling that of SELENKA's Pl. 17 fig. 11 and Pl. 18 fig. 2, on which my own interpretation, differing slightly from that of SELENKA was based.

From the figures here given, magnified about 150 times and obtained from consecutive sections of one blastocyst each, anybody may make plastic reconstructions in space. It can then not be denied that some of these blastocysts do contain an inner cell mass which in the case of fig. 1 to 5 was of the utmost regularity and composed of 16 cells. In most cases this mass is adherent at one spot to the trophoblast, as we notice it in Eutheria. It moreover strikes us that in fig. 1—4 the 16 cells seem to be imbedded in a sort of matrix, distinctly the same as is present in the preparation from which HILL has taken his fig. 37 and which he has there termed *cgl*, whereas in that case (of which I also give illustrations in fig. 7*a*—*d*) the one cell enclosed inside the blastocyst and designated by HILL by the letters *abn* (standing for abnormal) is yet single in contradistinction to the 16 cell stage just now described and figured. This one cell is not imbedded in, but in close contact with the mass *cgl*. I do not wish for the present to give a further description or interpretation of this matrix, which HILL designates as *coagulum* and which is also found in those blastocysts which he regards as normal and in which there is *no* cellproliferation inside the blastocyst-wall.

I cannot convince myself that the histological aspect of the enclosed cells would justify anyone to stigmatize them as "abnormal".

However, from the evidence at present available I am not going to conclude that, contrary to HILL's conviction, the blastocyst here figured are *normal* and that those which he regards as normal — and which though lacking any internal cell mass are more numerous — should be looked upon as *abnormal*. I am only pretending that a decision on this head is for the present moment *premature*, and that we must necessarily postpone its definite solution until the examination of a much larger batch of blastocysts of either Dasyurus or Didelphys has furnished us with a key to this riddle [1]).

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[1]) I may here remark that an attempt may be made to explain away the difficulties against a direct comparison between the "normal" and the "abnormal" blastocysts in assuming that in many cases of Dasyurus the embryonal knob cells arrange themselves in a flat layer without ever being overgrown by the unilaminar trophoblast wall (such as is also the case in all the reptiles and birds as far as

The other specimens here figured are developmental phases in which the same separation between an outer trophoblast and an inner cell-mass is also visible. Three of them are instructive as representing yet different stages from fig. 1—5.

In fig. 6*a*—*g* sections are figured in which an inner cellmass is *apparently* present. Close inspection shows that the cells which in fig. 6*b*—*e* appear to constitute an embryonic knob, at the same time form part of the outer surface of the blastocyst. Whether these very sections furnish arguments on which to conciliate HILL's interpretations with my own, must remain undecided for the present. Fig. 8 makes us acquainted with a blastocyst in which some two or three cells appear to be enclosed within an expanded trophoblast, but here again we may not look upon the specimen as decisive.

Fig. 9*a*—*d* represent a stage just a little earlier than that of fig. 1—5. The enclosed cells are imbedded in a similar matrix and also number about sixteen.

The size of the enclosed cells is intermediate to that of fig. 7 and 1—5. The distinction between trophoblast and inner cellmass is equally evident.

I finally mention, but do not figure, a somewhat later and considerably larger blastocyst, in which the cells that seem to represent the embryonic knob are histologically less perfect than those in fig. 1—4 and might raise doubts whether this particular specimen is or is not a link in a normal developmental series.

The facts which I have called attention to and which place us in the position of having to suspend our judgment with respect to fundamental support of HILL's theoretical speculations, prevent us *a fortiori* from weighing the respective merits of HILL's theoretical conclusions as compared to my own, and from entering into a debate such as he has opened in the article cited. It should not be lost sight of that just because the questions there raised are fundamental the discussions ought to be preeminently thorough and unprejudiced. The opposition with which my speculations on the first origin of the allantois have been met in different quarters is largely caused by that necessary sequel they lead to, viz. that *no* plausible phylogenetic explanation of the ventral stalk of the Primates and of the free allantois of other mammals and of the Sauropsids is possible as long as we hold on to the line of descent which is so emphati-

we know them), whereas in other cases these same cells undergo a certain amount of development within this wall and only later become intercalated among the trophoblast cells in the way they do so variedly in numerous Eutheria.

cally insisted upon by HILL and others: the derivation of viviparous mammals from oviparous ancestors, which were provided with an eggshell and had a free allantois.

The Prototheria (Ornithodelphia), to the embryology of which HILL has so largely contributed, are thus entirely out of the direct line of descent of all the other mammals. It is only natural that HILL should be a bit prejudiced on this particular point. He admits in his above-cited paper (p. 109 last paragraph) that the unilaminar blastoderm of the Prototheria is unmistakeably the trophoblast, but denies that the cells situated internally to that in the region of the white yolk bed are the mother-cells of the embryonic knob. I feel inclined to believe that the footnote on p. 1079 and the misunderstanding there explained away, will make him reconsider this denial and agree with me that also here we ought to suspend our judgment till more material is available.

I must finally point out that if my contentions on these last few pages concerning the phylogeny of the allantois may to some appear to be too provisional or unreserved I have just in hands and partly already in the press a description of the very early stages of Galeopithecus. In this mammal — the full description of which I hope will be published before the autumn — we find a representative of an order which is undeniably primitive, in the possession of developmental features that force us to conclude that in the very early stages it possesses a connective stalk (Haft- or Bauchstiel) between embryonal shield and trophoblast, whereas later on this stalk disappears in consequence of the development of the coelom and is gradually replaced in about the same situation by a free allantois, the origin of which may be traced to processes in the very matrix of the original connective stalk. This would be a direct argument from ontogeny favourable to my speculations and not explainable in any other way. I cannot however here do more than hint at it.

This paper might perhaps yet have harboured some amount of refutation of certain objections to my theoretical views that were advanced by MAC BRIDE in a paper on Amphioxus in No. 215 of the Q. J. (vol. 54). I refrain from doing so because in that case there are no positive facts upon which to base a rejoinder, as in the case of Prof. HILL's attack. Moreover, since it is patent that MAC BRIDE (l. c. p. 332) has failed to understand my own views about the phylogeny of the allantois to such an extent that he can present it as follows: "along the stalk of connection between embryo "and vesicle the bladder subsequently grew and so the allantois "was formed" any fruitful discussion on my phylogenetical speculations is excluded from the starting point. And I prefer to abide by Mac Bride's final jugdment, that: "Prof. Hubrecht has read the book "of Vertebrate development upside down" until an accumulation of facts on either side will have brought the balance into a position that will allow us to determine what is *up* and what is *down*.

EXPLANATION OF FIGURES.[1]

Fig. 1—5. Dasyurus N⁰. 7.

1*a*—1*c*. Three sections through blastocyst and shell. In *a* and *b* only trophoblastcells; in *c* the inner cell mass (embryonal knob?) enclosed in matrix (coagulum?).

Fig. 2 and 3. The two sections through the inner cell-mass immediately following that of fig. 1*c*.

Fig. 4*a*—*l*. Eleven consecutive sections through the above, numbered so as to enable us to reconstruct the mulberry shape.

Fig. 5. The actual reconstruction of the 16 cells composing the inner cellmass.

Fig. 6*a*—6*g*. Dasyurus N⁰. 11.

Six sections, of which *b*—*f* are actually consecutive, showing accumulation of massive cells in one blind corner of the blastocyst. It is closed at the other end in 26 consecutive sections situated before 6*a*; it is thus unilaminar. In 6*b* the eggshell is indicated.

Fig. 7*a*—*d*. Dasyurus N⁰. 12.

Sections through the same blastocyst and inner cell that have served for Prof Hill's fig. 37. The nucleus (?) of what Hill calls the coagulum has a very different character from that of the cell. 7*a* has its place in the series between 7*b* and 7*c*.

Fig. 8. Dasyurus N⁰. 9.

A section showing shell, trophoblast and two apparently independent cells inside the blastocyst.

Fig. 9*a*—*d*. Daysurus N⁰. 8.

Four sections through a blastocyst that has many points in common with that of fig. 1—5. The size of the cells of the inner cell-mass is intermediate between that of fig. 7*a* and fig. 1*c*; the number is also about 16; the matrix (coagulum) is less regular. The number of trophoblast cells is 62, they are less numerous than in fig. 1*c* where we count 192.

Fig. 10 and 11. Copies of two figures taken from Selenka's development of the Opossum (Wiesbaden Kreidel 1887) showing (fig. 10) Selenka's "Urentodermzelle" and (in fig. 11) the contrast between tropoblast and inner cell mass, the latter on the point of coming to the surface.

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[1] The number by which the Dasyurus are referred to in this paper refer to preparations which in Hill's collection are labelled as follows:

Dasyurus 7: 2,3. 16. VII. 01. * * 39
„ 8: 2*B*. 16. VII. 01. 39
„ 9: 46. Picro. abn. 29. 6. 04
„ 10: 45. Herm. abn. 29. 6. 04
„ 11: 45. Herm. * 29. 6. 04
„ 12: 2*B*. 16. VII. 01. 397.

Mathematics. — *"Quadratic complexes of revolution and congruences of revolution"*. By Dr. J. Wolff at Middelburg. (Communicated by Prof. Jan de Vries).

§ 1. The following treatise joins the investigation of Prof. Jan de Vries Proceedings Royal Acad. of Amsterdam Vol. IX 1906/7, p. 216—221).

If we choose the common centre O of the two quadratic surfaces of revolution O_1^2 and O_2^2, forming together the singular surface of a quadratic complex of revolution Ω, as origin of a rectangular system of coordinates, then the roots of $Ez^2 - 2Fz + A = 0$ must differ only in signs, the *bisingular points* B_1 and B_2 where O_1^2 and O_2^2 touch each other corresponding to those roots. Then we have $F=0$, so that the equation of Ω becomes

$$A(p_1^2 + p_2^2) + Bp_3^2 + 2Cp_3p_6 + Dp_6^2 + E(p_4^2 + p_5^2) = 0 \quad . \; . \; (1)$$

This equation can be written in each of the forms

$$E\left(p_4 + p_1\sqrt{\frac{A}{E}}\right)^2 + E\left(p_5 + p_2\sqrt{\frac{A}{E}}\right)^2 + $$
$$+ Bp_3^2 + 2(C + \sqrt{AE})\,p_3p_6 + Dp_6^2 = 0, \quad . \quad . \quad (2)$$

$$E\left(p_4 - p_1\sqrt{\frac{A}{E}}\right)^2 + E\left(p_5 - p_2\sqrt{\frac{A}{E}}\right)^2 + $$
$$+ Bp_3^2 + 2(C - \sqrt{AE})\,p_3p_6 + Dp_6^2 = 0 \quad . \quad . \quad (2^*)$$

As the first members of (2) and (2*) can be reduced to four squares, thus also to 2 products, out of each of the equations (2) and (2*) two systems of congruences (1,1) can be deduced, out of which Ω is built up; we call them Γ and Γ', resp. Γ^* and Γ'^*. Each Γ has a regulus in common with each Γ'; likewise each Γ^* with each Γ'^*. The directrices of all those congruences form O_1^2 and O_2^2.

§ 2. We apply to the xOy-plane a screwing around Oz of which the angular velocity counted positively from Ox to Oy is in a ratio to the translation velocity as $1 : k$. We choose the right lines p_1 and p_2 along which coincide the velocities of two arbitrary points P_1 and P_2 lying in xOy as directrices of a congruence $\Gamma(1,1)$ in order to find the equation of the complex which originates when Γ revolves about Oz.

Let OP_1 be equal to a_1, $OP_2 = a_2$, $\angle xOP_1 = \Phi$, $\angle xOP_2 = \Phi + \alpha$.

The coordinates of p_1 are in order of succession of the indices:

$$a_1 \sin \Phi,\ - a_1 \cos \Phi,\ - k,\ ka_1 \sin \Phi,\ - ka_1 \cos \Phi,\ a_1^2\,;$$

those of p_2 are deduced from these by substituting a_1 for a_2 and

$\Phi + \alpha$. for Φ. A ray of the complex to be found is represented by the equations

$$(p_4 + kp_1)\sin\Phi \qquad - (p_5 + kp_2)\cos\Phi \qquad = \frac{k}{a_1}p_6 - a_1 p_3$$

and

$$(p_4 + kp_1)\sin(\Phi + \alpha) - (p_5 + kp_2)\cos(\Phi + \alpha) = \frac{k}{a_2}p_6 - a_2 p_3.$$

Elimination of Φ furnishes as equation of the complex:

$$(p_4 + kp_1)^2 \sin^2\alpha + (p_5 + kp_2)^2 \sin^2\alpha =$$

$$= \left(\frac{k}{a_1}p_6 - a_1 p_3\right)^2 - 2\left(\frac{k}{a_1}p_6 - a_1 p_3\right)\left(\frac{k}{a_2}p_6 - a_2 p_3\right)\cos\alpha + \left(\frac{k}{a_2}p_6 - a_2 p_3\right)^2 \quad (3)$$

Equation (3) represents the complex Ω when the following five relations have been satisfied:

$$\sin^2\alpha \qquad = \lambda E \quad \ldots\ldots\ldots \quad (4)$$

$$k \qquad = \pm\sqrt{\frac{A}{E}} \quad \ldots\ldots \quad (5)$$

$$a_1^2 - 2a_1 a_2 \cos\alpha + a_2^2 \qquad = -\lambda B \quad \ldots\ldots\ldots \quad (6)$$

$$\frac{k^2}{a_1^2 a_2^2}(a_1^2 - 2a_1 a_2 \cos\alpha + a_2^2) = -\lambda D \quad \ldots\ldots\ldots \quad (7)$$

$$k\left\{-2 + \left(\frac{a_1}{a_2} + \frac{a_2}{a_1}\right)\cos\alpha\right\} \qquad = -\lambda(C \pm \sqrt{AE}). \quad \ldots \quad (8)$$

Equation (5) furnishes two values for k differing only in sign; the absolute value is $\sqrt{-OB_1^2} = \sqrt{-OB_2^2}$. From (6) and (7) ensues:

$$a_1 a_2 = \sqrt{\frac{AB}{DE}}, \quad \ldots\ldots\ldots \quad (9)$$

out of (8) in connection with (4), (5), and (6):

$$\cos\alpha = \frac{a_1 a_2 (C - kE)}{kB} \quad \ldots\ldots\ldots \quad (10)$$

For each k we find *one* value of $\cos\alpha$. As however all conditions remain satisfied when α changes signs, we may add to P_1 instead of P_2 also the image P_2' of P_2 with respect to OP_1. Out of (4) follows for every k *one* λ; finally we find a_1 and a_2 out of (6) and (7); they are the radii of the circles according to which xOy is cut by O_1^2 and O_2^2. By division of (4) and (7) is evident, that the distance from O to $P_1 P_2$ (or $P_1 P_2'$) must be the same for both values of k. This was to be foreseen; $P_1 P_2$ must touch, being a complex ray, the complex conic of xOy, being a circle with O as centre. Its radius is:

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$$r = \sqrt{\frac{-A}{D}} \quad . \quad . \qquad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

§ 3. To fix our thoughts we suppose that A and E have the same signs.

For $k = +\sqrt{\frac{A}{E}}$ to each ray p_1 of the regulus R_1 wound to the right lying on O_1^2 two rays p_2 and p'_2 are conjugated of the regulus R_2 wound to the right lying on O_2^2, so that $\angle P_1OP_2 = \angle P'_2OP_1 = \alpha$. The complex $\boldsymbol{\Omega}$ is originated by revolution about Oz of the congruence $\boldsymbol{\Gamma}$ with the directrices p_1 and p_2 as well as of $\boldsymbol{\Gamma}'$ with directrices p_1 and p'_2.

For $k = -\sqrt{\frac{A}{E}}$ to each ray p_1^* of the regulus R_1^* wound to the left lying on O_1^2 are conjugated two rays p_2^* and p'^*_2 of the regulus R_2^* wound to the left lying on O_2^2, so that the points of intersection of p_1^* and p_2^* with xOy as well as those of p_1^* and p'^*_2 are seen from O under an angle α^*. The complex $\boldsymbol{\Omega}$ originates by revolution of the congruence $\boldsymbol{\Gamma}^*$ with directrices p_1^* and p_2^* as well as of $\boldsymbol{\Gamma}'^*$ with directrices p_1^* and p'^*_2.

Let the right line P_1P_2 be cut by O_1^2 still in Q_1, by O_2^2 in Q_2. Through Q_1 pass the rays q_1 and q_1^* of R_1 and R_1^*, through Q_2 pass the rays q_2 and q_2^* of R_2 and R_2^*. We then find that $\boldsymbol{\Omega}$ is built up in four ways out of systems of ∞^1 congruences (1,1), which are originated in the following manner:

1. by revolution of $\boldsymbol{\Gamma}$ with directrices p_1 and p_2, 2. by revolution of $\boldsymbol{\Gamma}'$ with directrices q_1 and q_2, 3. by revolution of $\boldsymbol{\Gamma}^*$ with q_1^* and p_2^*, 4. by revolution of $\boldsymbol{\Gamma}'^*$ with p_1^* and q_2^*.

If $C = 0$, then from (10) follows that $\alpha^* = \alpha$ and as p_1^* and p_2^* are then the images of p_1 and p_2 with respect to xOy, then $\boldsymbol{\Omega}$ is proof against reflection to xOy, thus *symmetric*.

§ 4. Let A_1 be a point of p_1. The complex cone of A_1 consists of the planes (A_1, p_2) and (A_1, p'_2), the singular ray s starting from A_1 rests upon p_2 and p'_2. If A_1 describes the right line p_1, then s describes the regulus ϱ_1, of which the system (p_1, p_2, p'_2) is the conjugate one. As p_1, p_2 and p'_2 belong to reguli wound to the right on O_1^2 and O_2^2 and these surfaces touch each other in B_1 and B_2, we find that p_1, p_2 and p'_2 are cut by two isotropic lines B_1I and B_1J, at right angles to Oz so that I and J are the circlepoints of xOy. If thus we bring through *one* ray s of ϱ_1 the linear complex C_1 having Oz as axis, then ϱ_1 lies entirely inside C_1, having s, B_1I

and $B_2 A$ in common with it. When revolving about Oz we find that ϱ_1 remains in C'_1 and so the section of C'_1 with Ω forms a congruence of revolution (2,2). If A_1 describes a right line p_1^*, then s describes a regulus ϱ_1^*, which generates by revolution the same congruence as ϱ_1.

The singular rays starting from the points A_2 of O_2^2 form a suchlike congruence. *The singular rays of* Ω *form therefore two congruences of revolution* (2, 2).

§ 5. A congruence of revolution C (2, 2) is generated when Ω is cut by an arbitrary linear complex having Oz as axis:

$$p_6 + mp_3 = 0 \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

If we replace in (1) p_6 by $-mp_3$, we get:

$$A(p_1^2 + p_2^2) + B'p_3^2 + E(p_1^2 + p_5^2) = 0, \; . \; . \; . \quad (13)$$

where $B' = B - 2Cm + Dm^2$.

We easily find for the focal surface:

$$AE(x^2 + y^2)^2 + B'(x^2 + y^2)(A + Ez^2) + m^2(A + Ez^2)^2 = 0 \quad (14)$$

So it consists of two quadratic surfaces of revolution F_1^2 and F_2^2. which touch each other in the same points B_1 and B_2 as O_1^2 and O_2^2. Intersection of $p_6 - mp_3 = 0$ with the invariable complex (13) furnishes a congruence with the same focal surfaces F_1^2 and F_2^2. The common tangents of F_1^2 and F_2^2 form therefore two quadratic congruences of revolution, which are each other's images with respect to xOy.

§ 6. Let a ray s of the congruence cut the planes β_1 and β_2, which are in B_1 and B_2 perpendicular to Oz, in $P_1\left(x_1, y_1, -\sqrt{\frac{-A}{E}}\right)$ and $P_2\left(x_2, y_2, +\sqrt{\frac{-A}{E}}\right)$. If we express the coordinates of s in x_1, y_1, x_2 and y_2 and if we then substitute them into (12) and (13), we arrive at:

$$x_1 y_2 - x_2 y_1 = 2m\sqrt{\frac{-A}{E}} \; . \; . \; . \; . \; . \; . \; . \quad (15)$$

and

$$x_1 x_2 + y_1 y_2 = -\frac{AB'}{E} . \; . \; . \; . \; . \; . \; . \; . \; . \quad (16)$$

The rays s of the congruence therefore determine a correspondence (1, 1) between the points of the planes β_1 and β_2. If P_1 describes a ray of the pencil (B_1, β_1) then P_2 describes a ray of the pencil

(B_2, β_2) and s describes a regulus Σ. To B_1 corresponds the point at infinity of B_2P_2, to B_2 that of B_1P_1, so that in Σ are lying the rays through $B_1 // B_2P_2$ and through $B_2 // B_1P_1$. From this ensues that Σ touches β_1 and β_2 in B_1 and in B_2 so that Oz is an axis of symmetry of Σ and O the centre.

So a congruence of revolution (2,2) *is generated by the revolution of a regulus about one of its axes of symmetry.*

If only real congruences are taken into consideration, the two kinds can be distinguished:

1. The regulus revolves around an axis of symmetry not cutting it; then the focal surfaces are one-sheeted hyperboloids of revolution.

2. The regulus revolves around an axis of symmetry cutting it; then one of the focal surfaces is an ellipsoid of revolution, the other a two-sheeted hyperboloid of revolution.

In the former case the contact of F_1^2 and F_2^2 and the regulus Σ takes place in imaginary points, in the latter case in real points.

In both cases the sections of xOy with F_1^2 and F_2^2 consist of circles having as radii the axes of symmetry of Σ lying in xOy. *One* of them is imaginary in the second case.

Physics. — *"Observations concerning anomalous dispersion of light in gases."* (First communication). By Prof. W. H. Julius and B. J. van der Plaats.

Although it be now generally admitted, that anomalous dispersion of light must influence certain astrophysical phenomena in some degree, yet the majority of astrophysicists opine, that such influence cannot bear a general or radical character, but may in some special cases only, near a few lines of the spectra of celestial bodies, perhaps become apparent.

In order to make out whether that opinion is tenable, one has to answer two questions. First: Is anomalous dispersion an exceptional or a *general* phenomenon, appearing in the vicinity of every absorption line — provided that the conditions of the observation are properly chosen? And secondly: Does the present state of physical and astrophysical knowledge make it very probable or not, that in the atmospheres of celestial bodies conditions prevail, from which the appearance of quite conspicuous effects of anomalous dispersion necessarily follows?

In this paper we are not going to consider the second question;

it has been treated of on several occasions already [1]), and will also in the future continue to form a subject of close investigation.

As to the first question, we notice that the dispersion theory has settled it to a certain extent. According to that theory there is a necessary correlation between selective absorption and the rapid variation of the index of refraction for waves differing little in length from the absorbed waves. The whole of experimental evidence supporting the dispersion theory in general, may thus be considered to plead in favour of the thesis, that really every absorption line involves anomalous dispersion of neighbouring waves. The hypothesis that many solar phenomena are perhaps produced by anomalous dispersion, could therefore not be deemed unfounded or premature even in 1900, when introduced by one of us [2]), although at that time the peculiar course of the index of refraction near narrow absorption lines, had really been observed with very few metallic vapours only. Direct observations have considerably accumulated since then. From researches by LUMMER, PRINGSHEIM, WOOD, EBERT, SCHÖN, PUCCIANTI, GEISLER, LADENBURG, and others, we know that hundreds of lines determine variations in the velocity with which neighbouring kinds of light are propagated, exactly in the manner as required by the dispersion theory.

The degree in which the phenomenon showed itself was very different for different lines, and entirely dependent, of course, on the conditions of the experiment. With innumerable lines it has not yet been observed at all. But in view of the well-established dispersion theory the supposition that certain absorption lines or absorption bands give *no* anomalous dispersion [3]), is a more hazardous one, than the supposition that the phenomenon will manifest itself as soon as we shall have realized the proper conditions.

We propose to investigate those conditions for a number of gases and vapours, and to inquire whether selective absorption really is always accompanied by anomalous dispersion, as the theory demands, or whether there are exceptions, which would make a correction of the theory unavoidable.

The observations to be described briefly in this paper bear upon iodine vapour, bromine vapour, and nitrogen peroxide. We used the

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[1]) Proc. Roy. Acad. Amsterdam, XII, 266 and 466 (1909), XIII, 2 and 881 (1910/11). Les raies de Fraunhofer et la dispersion anomale de la lumière. Le Radium VII, Oct. 1910.

[2]) Proc. Roy. Acad. Amsterdam, II, 575, (1900).

[3]) Cf. e.g. HALE and ADAMS, Astroph. Journ. **30**, 230, 1909.

method first applied to similar researches by PUCCIANTI [1]), then by GEISLER [2]). As our present equipment bears a temporary character, and we expect to dispose of better appliances at a later date, the following short description of the apparatus used may suffice.

The light coming from an arc lamp of 25 A. passes through a JAMIN interferential refractor, by which it is split up into two beams, 29 millimeters apart. On the path of one of the beams there was a glass tube, 12 centimeters in length, into which a controlable quantity of bromine vapour or of nitrogen peroxide could be introduced, while the other beam traversed two pieces of plate glass, identical with the ones shutting the tube. With both gases observations were made at the temperature of the room. Iodine vapour, on the contrary, was examined at 53° C. For that purpose two equal glass tubes, 40 c.m. long, were placed one in each beam, a HERAEUS electric furnace enveloping them both, so that their middle parts, for a length of 23 c.m., could be evenly heated to the same temperature. One of the tubes contained some iodine. They both communicated with the open air by narrow side-tubes.

By means of lenses the horizontal interference-fringes were focussed on the slit of the spectrograph. As a low dispersion apparatus we used a HILGER constant deviation spectrograph, with one dense flint prism; a few observations were made with high dispersion apparatus, consisting of a ROWLAND plane grating (working surface 8 × 5 c.m., 5680 lines to the c.m.), two silvered glass mirrors of 150 and 250 c.m. focal distance respectively, and camera.

The annexed plate shows threefold enlargements of some of the spectrograms. Much detail is lost in the reproduction. When there was no selectively absorbing substance present in one of the beams, the interference fringes were perfectly smooth and almost horizontal, apart from their fanlike spreading with increasing wavelength. As soon as the absorbing gas is introduced, the velocity of certain waves has increased on the one path, of other waves diminished; so the fringes suffer local displacements, quickly increasing as we approach an absorption line, and thus show very intricate incurvations. In our arrangement a *downward* incurvation of the fringes means increasing velocity of the corresponding waves in the vapour, and therefore, decreasing index of refraction of the latter; an *upward* incurvation of course indicates the reverse.

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[1]) PUCCIANTI, Mem. Spettr. Ital. **33**, 133, 1904; Nuovo Cimento, Ser. V, Vol. IX, 303 (1905).

[2]) H. GEISLER, Zur anomalen Dispersion des Lichtes in Metalldämpfen, Diss., Leipzig, Barth, 1909.

The first and second spectrum give the anomalous dispersion and the absorption in *iodine vapour*. Proceeding in the direction of increasing wave-lengths towards the sharp edge of any absorption band, we see the fringes curve steeply down, which proves that the index of refraction is quickly diminishing; within the absorption band the index appears to increase, rather quickly at first, then slowly [1]), until in approaching the next band it again falls off steeper and steeper. This process repeats itself at every fluting, without exception.

The resolving power of the HILGER spectrograph was not sufficient to permit of distinguishing the separate lines composing the flutings of the iodine spectrum; but by analogy with quite conspicuous phenomena observed in the case of nitrogen peroxide (as will soon appear), it can hardly be doubted that also in the iodine spectrum each line of a fluting causes the index of refraction to sink on its violet side, to rise on its red side, and that the apparently continuous increase of the index within each fluting results from the joint action of the anomalies, due to the separate lines of that fluting. This interpretation — which is in keeping with the dispersion theory -- is strongly supported by the results of our observations on nitrogen peroxide.

With *bromine vapour* we did not succeed in photographing equally sharp and distinct anomalies of the dispersion as those obtained with iodine. This may perhaps be due to the fact that, if one compares such quantities of both vapours as will transmit nearly equal fractions of the incident light, the intensity varies less within the bromine flutings than within the iodine flutings. With equal average absorption there are stronger contrasts in the spectrum of iodine, than in that of bromine vapour. Nevertheless, on examining the third and fourth spectrum, we may safely conclude that the anomalous dispersion in bromine vapour bears entirely the same character as that in iodine vapour.

The next three spectra relate to *nitrogen peroxide*: the absorption spectrum (photographed while one of the interfering beams was screened off) is placed between two spectra showing the anomalous dispersion; number 5 was obtained with gas of lower, number 7 with gas of higher density. Exposure and development were so timed, that on the one photograph the region between λ 4400 and λ 5200, on the other that between λ 5200 and λ 6200 comes out to advantage. Among the hundreds of lines visible in the NO_2-spectrum we could not find a single exception to the rule, that every

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[1]) Cf. H. GEISLER, l. c., p. 24.

absorption line produces a local shift of the interference fringes. The amount of the shift depends, of course, on the quantity of gas traversed. In spectrum 5 e.g. the dispersion anomalies are scarcely perceptible in the red; they increase in the main with decreasing wave-length (as also the absorbing power of NO_2 increases in the main toward the violet); in spectrum 7, the quantity of gas being greater, we observe very conspicuous anomalies already in the red, and when proceeding toward smaller wave-lengths, see them so much increase, that beyond λ 5000 anything like horizontal fringes has disappeared.

At a few places, where more or less isolated lines occur, it is clearly visible that the adjacent light shoots out into the next fringes like sharp spikes, upward on the red side, downward on the violet side of the line. Now, if we suppose the same phenomenon to repeat itself near each of the many narrow lines which, crowded together, constitute a band or fluting in the spectrum, we must expect to find the dark fringes less dark, the bright fringes less bright in any region corresponding to a band or fluting. This particularity is indeed very conspicuous on the original photographs. Where broad dark bands occur in the absorption spectrum, the system of fringes shows somewhat vague, contrastless; whereas light and dark distinctly alternate in the system, wherever the average absorption is small.

Besides, we observe that in every region crowded with absorption lines, the mean index of refraction rises with increasing wave-length, and that in regions with few lines it sinks.

The strips 8 and 9 on the plate show parts of the NO_2-spectrum with high dispersion. Number 9 is an original-size reproduction[1]), covering the part of the spectrum which, on 7, is enclosed between *a* and *d*; of this a part again (lying between *b* and *c*) is given on a three-fold scale in strip 8.

As in this case, for want of intensity, the time of exposure had to be about one hour and a half, and because the arrangement had no claim to perfect stability, the details are not so sharp on the photograph as they showed visually. But on direct observation many bands were now resolved into fine lines, and there could be no doubt that each line clearly influenced the refractive index for adjacent waves. Even the reproduction offers the required evidence. Indeed, every absorption line of nitrogen peroxide visible on it has

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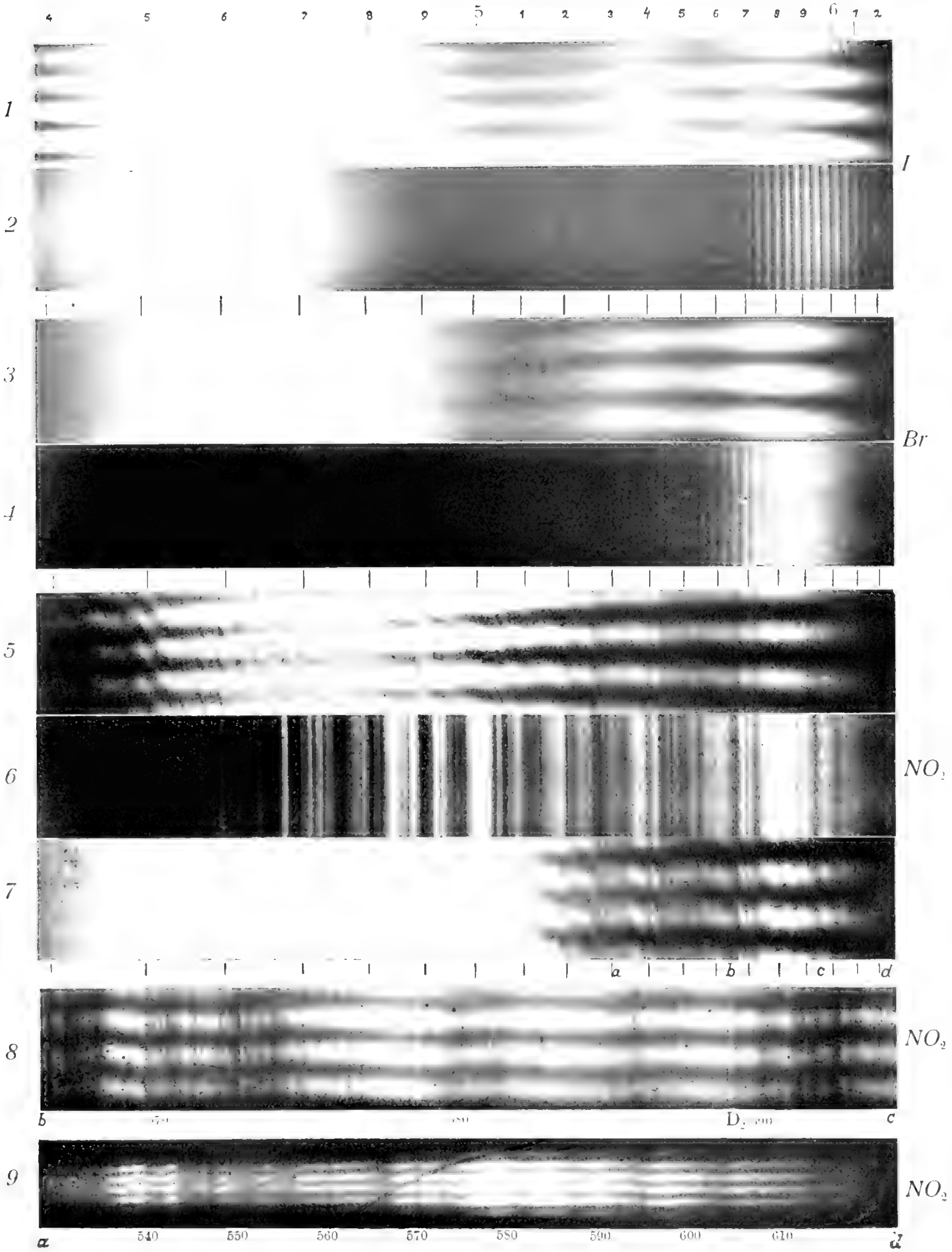
[1]) The fringes are there curved in the opposite direction (as compared with the other spectra on the plate), owing to a slight alteration in the arrangement of the apparatus.

W. H. JULIUS and B. J. VAN DER PLAATS. "Observations concerning anomalous dispersion of light in gases".



a serpentine shape, owing to the fact that each bright interference fringe, at its intersection with a dark line, seems to push it toward the right at the lower edge, toward the left at the upper edge of the fringe. This proves that the darkness of those lines is not exclusively caused by absorption, but partly by anomalous dispersion. The serpentine shape of the lines is not an optical illusion, for the sodium line D_2 (D_1, which lies at $2^1/_2$ m.m. distance to the right, is invisible on the reproduction), originating in the arc, is sharp and perfectly straight. So we may take it for etablished by experiment, that thousands of lines occurring in the spectra of iodine vapour, bromine vapour, and nitrogen peroxide, produce anomalous dispersion of the waves lying close to them.

The result of this investigation supports the thesis, that selective absorption is always accompanied by anomalous dispersion.

Physics. — "*Further experiments with liquid helium.*" By Prof. H. KAMERLINGH ONNES. Communication N°. 119 from the Physical Laboratory at Leiden.

(Communicated in the meetings of Dec. 24, 1910 and February 25, 1911).

A. *Isotherms of monatomic gases etc.* VIII. *Thermal properties of helium.*

§ 1. *The helium-bath.* In most of the experiments that one would like to make at helium temperatures, it is necessary to transfer the liquid helium from the apparatus in which it has been prepared to another — the helium cryostat — more suitable for holding the apparatus arranged for these special experiments. In Comm. N°. 112 (June 1909) it was mentioned that this was going to be tried; and in the Jubilee book presented to J. M. VAN BEMMELEN it was further stated that the transference had, in fact, been once successfully accomplished. Although the success which attended this operation allowed immersion in the protected helium bath of the apparatus, with which it was shown that even at a vapour pressure as low as 0.15 mm. helium is still a liquid, it was nevertheless evident that this desirable result had been obtained only by accident. A method that promises to be more efficient is now being developed, and I hope to be able to make a communication in the near future concerning it.

In the meantime, a few problems could already be studied with the help of a liquefying apparatus resembling the original liquefying apparatus (Comm. N°. 108, Proc. of May/June 1908) sufficiently well to ensure that when an experimental apparatus is introduced into its its interior this experimental apparatus would also be surrounded with liquid helium. To be certain that this was the case, it was necessary that the principle of the original liquefying apparatus should not be altered in any way; and, hence, the difficulty that the liquid helium would be contained in a space that is practically closed above by the regenerator spiral could not be avoided. But this space destined to contain the liquid helium could still be made as large as was found permissible from the experience gained with the liquefying apparatus. An apparatus was, therefore, constructed to hold a thermometer reservoir of greater dimensions than the one which had been used up till 1909, a resistance thermometer such as was used in the investigation of the electrical resistance at hydrogen temperatures, a dilatometer of dimensions greater than those given in Comm N°. 112, and also a control dilatometer.

The apparatus is shown in Fig. 1 Pl. I [1]. The letters are the same as in Pl. III of Comm. N°. 108, and are accented where one of the parts has been modified. Moreover, Pl. II of that Communication holds for the helium cycle as far as its use at ordinary pressure is concerned. To allow the helium to evaporate under lower pressure the tube that leads the gas off from the liquefier is coupled to the wide exhaust of a BURCKHARDT vacuum pump capable of transplacing 360 m.^{3} per hour. To follow this operation the part D_a and those attached to it in Pl. II Comm. N°. 108 must be replaced by the modifications shown in Pl. II fig. 1; connection with the pump is made through $E_a V_a$ and this is closed by the tap 22; while 23 in a bypass allows a fine adjustment of the quantity of the gas that is being removed; 24 and 25 allow the gasometer and the liquefier to be independently evacuated (see Pl. II Comm. N°. 108).

Besides the changes in the apparatus necessary to enable it to contain the measuring apparatus, it remains to be remarked that a second helium thermometer Na_1, Na_2, Na_3, now serves to indicate the quantity of liquid hydrogen present in F instead of the two thermocouples that were formerly used in conjunction with the small helium thermometer (now N'_1, N_2, N_3). The position of the liquid surface in F can be ascertained much more easily from the motion of the mercury in the capillaries N_3 and Na_3 than was possible with the more round-about thermocouple measurements; the liquid hydrogen can therefore be used more sparingly, and the tedious preparatory work of adjustment necessary for these experiments can be shortened.

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[1] The alcohol glass with its attachments (cf. Pl. III, Comm. N°. 108) Ea is only partially shown in the drawing.

In the lower part — the cryostat space — of the glass E'_a (Fig. 1 and Fig. 2) is the reservoir Th' of the helium thermometer, with which the temperature of the bath is determined, the resistance Ω, the dilatometer Δ, and the control apparatus of the dilatometer δ. And finally, a thick copper rod Cu is also placed in it so that, since the liquid in the bath cannot be stirred, conduction along the rod may keep the temperature of the bath more equable at all points. The narrow space between the regenerator spiral A and the wall of the vacuum glass E'_a is filled with flannel, and now three capillaries pass through it instead of the single thermometer capillary (that of Th_1 Pl. III Comm. N°. 108). One of these, Th'_2, leads to the thermometer (replacing Th_1, Th_2, Th_3, Th_4, of Pl. III, Comm. N°. 108), the second to the dilatometer (this was already used in Comm. N°. 112), and the third to the control apparatus of the dilatometer (connecting δ with W). Furthermore, instead of the two insulated wires of the thermocouple (Comm. N°. 108) four insulated wires Wa_1, Wa_2, Wb_1, Wb_2, now pass through this space; these are the pairs of wires that lead the current to and from the resistance Ω.

All these capillaries and insulated wires must pass through the space that is filled with liquid air, which must still remain airtight (this space is described under d of Comm. N°. 108 § 2, and b Pl. II of that Comm. shows how liquid air is introduced). This is accomplished by soldering the capillaries to the new-silver wall of the liquid air vessel, while the insulated leads are enclosed in new-silver tubes that pass through the wall and are soldered to it.

The operation of filling the lower portion E_{a1} (Pl. I fig. 1) with liquid helium is conducted in exactly the same way as is described in § 4 Comm. N°. 108. Practice in the various operations and the improvement made by introducing the second helium thermometer rendered it possible to save a fair amount of liquid hydrogen so that, as a part of the necessary hydrogen had been liquefied the previous day, it was possible to begin at half past seven in the morning and have the cryostat part of the apparatus full of liquid helium by a quarter to two in the afternoon. The circulation pressure was kept at 25 atmospheres (cf. § 2, Comm. N°. 112).

The pressure under which the helium vaporizes is derived from the pressure obtaining in the wide space beneath the german silver chamber F; from this space a tube passes through F and comes outside the apparatus at p_1; it is there coupled to the apparatus for regulating and measuring the pressure. The difference of pressure between this space and the surface of the liquid helium necessary to drive the vapour up between the coils of the regenerator spiral was found, from measurements made with air, to be less than $^1/_{20}$ mm., and may, therefore, be left out of account. Only at very low pressures will a correction be necessary for it in obtaining very accurate results.

Fig. 2, Pl. II shows the apparatus that serves to regulate the quantity of gas pumped off through the exit valves; by such regulation the temperature of the cryostat part of the apparatus is kept as constant as possible, and from its constancy one can judge how far the vapour pressure remains invariable; it also shows how this pressure is measured. For pressures greater than 5 cm. the gauge I_1 is used, for pressures between 5 cm. and 1 cm. I_2, and for pressures lower than 1 cm. I_3. By opening K_{i21}, K_{i22}, K_{i23}, or K_{i31}, K_{i32}, K_{i33}, I_{2a} or I_{3a}, as the case may be, is brought to a definite pressure, which is measured by I_1 or by the MAC LEOD gauge I_4; K_{i21} or K_{i31} is then closed, and the taps regulating the rate at which the gas is pumped off are operated so that the oil in the graduated sloping tubes of the indicators remains at the same mark.

Any definite pressure and, therefore, any definite temperature at the surface of the liquid in the cryostat can be quite satisfactorily obtained. The temperature of the bath, however, is less assured, since stirring is not possible, and the conductivity of *Cu* offers but slight compensation for this defect. The lower parts of the bath are at a higher temperature, and the corresponding vapour pressure may be increased by 0.009 to 0.011 mm. of mercury per mm. distance from the surface of the liquid helium; at the lowest temperatures this is equivalent to a temperature difference of 0.06 degree, and with this uncertainty we must be content as long as we have not at our disposal a cryostat in which stirring is possible; it is not, however, greater than uncertainties arising from other causes that are already present.

§ 2. *The Thermometer.* Temperatures were measured by means of a constant volume helium thermometer of zero pressure = 14.5 cm. (Cf. Comm. N°. 112).

At the lowest measured temperature, the pressure of the gas in the thermometer was 1.2 mm., and the vapour pressure of the helium was only 2 mm. The circumstances of measurement were, therefore, pretty much the same with respect to helium as if a constant volume ether vapour thermometer were used for determining ordinary atmospheric temperatures. In the present case there is, moreover, the particularly small value of the pressure itself to be taken into account. Hence, in the very nature of the determinations themselves there is cause for many uncertainties. In the meantime however, it seems best to make a beginning by assuming that the ordinary gas laws may still be applied at these densities, and to postpone the application of corrections for the deviations that should follow according to the law of corresponding states and for possible condensation of vapour on the walls, etc., until experiments have been completed which will afford an estimate of these corrections. In this way one can at least attempt to obtain data concerning certain thermal properties of helium. I mentioned in Comm. N°. 112 that at that time I had not been successful in overcoming the difficulties that are always encountered when making measurements with a thermometer, built on the principle of the one that has hitherto been used, in the immediate neighbourhood of apparatus that are used for the preparation of liquid helium. These difficulties have not yet been wholly removed. The necessity for simplicity and ease of manipulation of the apparatus, and the fact that the thermometric measurements should be independent of all vibration and all disturbances are difficult to reconcile. But still, it would appear that the temperatures obtained may be relied upon to within 1/10th of a degree.

The part of the helium thermometer that serves for the adjustment of the constant volume, and for the reading of the pressure is shown on the right hand side of Plate I. Its arrangement is similar to that of the hydrogen thermometer shown on Plate I of Comm. N°. 95*e* (Oct. 1906) when this is being used for measuring hydrogen temperatures; part of the lettering is chosen so as to correspond with that of the latter plate. On account of the smallness of the pressures to be measured at the helium temperatures the space above the mercury in the adjustable double manometer tube l and f_a is evacuated, and, to make quite certain, they are connected to an evacuated tube L filled with charcoal and immersed in liquid air. The manometer tube on which the pressures are read off, has, as well as the adjusting tube, a small steel point, so that the difference of level between the two mercury menisci may be obtained with greater accuracy. The base e_a which carries the point f_a is slitted, as can be seen in the figure. Before making any adjustments the tap K_{ϑ_3} is closed, and it is opened to allow communication between the mercury in the reading tube and that in the adjusting tube of the manometer only after the mercury meniscus in the adjusting tube has been brought to the level of the point f_a in the reading tube by opening K_{ϑ_1} and moving the double manometer tube up and down until this is accomplished. Then to proceed to an adjustment the adjusting tube can be shut off with K_{9_4}. By a slight turn of the screw s_e and of the screw with which the fine adjustment of the height of the manometer tube is obtained, both of which are within the observer's reach, the mercury surfaces are brought as near as possible to the two points; the height of the mid point between each point and its mirror image is then ascertained with the cathetometer provided with one of the reading microscopes of Comm. N°. 85 (April 1905) and of Comm. N°. 95*b* (Sept. 1906) when the cathetometer was used as a vertical comparator.

In this way, taking account of the indication of the sensitive levels, heights may be measured accurately to within 0.002 mm. To eliminate the uncertainty in the correction for the refraction of light through the glass at the place where the point is under observation and that in the correction for the temperature of the equilibrating mercury columns (as the capillary depression is only 0.01 mm. the uncertainty in it may be neglected) the tap K_{9_0} is introduced, and the spherical vessel d_5 forms part of the dead space [1]). If K_{9_0} is closed, and the mercury that stood in the narrow stem d_4 while the thermometer was being adjusted with K_{9_8} closed, is allowed to sink, there remains in the dead space only a very small and definitely known fraction of the total pressure, and the adjusting tube of the manometer must be lowered so as to bring the mercury levels once more to the two points. The displacement is read on a finely divided scale attached to the adjusting tube of the manometer, and at once gives in mm. of mercury the thermometer pressure for the temperature of the adjusting space, to which the only correction to be applied is that for the pressure remaining over.

We need not stop to describe the different devices (cf. Comm. N°. 60, Sept. 1900) by means of which the various points to be seen are so arranged that they can be brought in succession in sharp focus into the field of the cathetometer; the significance of the air-traps in the mercury filled connecting tubes is sufficiently obvious from the figure, as is also that of the mercury filled rubber tube *Sa* surrounding the rubber connecting tube *S* and its junctions with the other tubes. On account of the comparatively large value of viscosity, equilibrium is, in general, reached but very slowly between spaces occupied by gas at such low pressures as those obtaining in our thermometer reservoir and in the dead space. In the present

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[1]) A coupling is inserted in the capillary d_2 by means of which many operations and controls are much more easily accomplished; it allows the whole manometer part of the arrangement to be loosened, and either that or the remaining apparatus may be connected independently with an air-pump, etc.

instance, however, the favourable circumstance arises that only a very small quantity of gas has to flow over, seeing that the dead space is extremely small. Against the widening of the capillary it may be urged that then the quantity of gas contained in it would lead to inaccuracy owing to the uncertainty existing regarding the distribution of temperature along it. After full consideration of the change of viscosity and density with temperature, and also of constructional difficulties, the low temperature portion of the capillary was made of 37 cm. steel capillary of 0.5 mm. bore, and the part that is at practically room temperature was made of 50 cm. copper capillary of 1.0 mm. bore. The resulting uncertainty is, then, at the most, 1 $^0/_0$, while the viscosity is not yet excessive, seeing that it is possible to adjust to 0.01 mm. within a period of 2 minutes.

§ 3. *Densimetric Apparatus.* The part of the dilatometer that was immersed in the helium bath consisted of a reservoir Δ_1 with a stem $\angle_2$, a narrow glass capillary Δ_3 continued by a steel capillary. The mass of helium here present was determined volumetrically in the bulb V_1 with a graduated stem both above and below, whose temperature was determined by that of the surrounding water bath; the pressure was read on a scale by using the branch V_{2b} of the mercury reservoir V_2. The dimensions of Δ_1 and V_1 are so chosen that the position of the mercury for the desired pressure can be read on the lower part of V_1's graduated stem before the dilatometer has been filled, and on the upper part after the filling has taken place. Moreover, the cross-section of the graduated stem has been chosen of such a size that when the dilatometer has been cooled again with $K_{\Delta v}$ and $K_{\Delta w}$ closed, after filling it at the boiling point to above the mark, the meniscus still remains in the stem even at the greatest densities employed.

Although the capillary is very narrow at the part where its temperature is uncertain, the correction for the gas condensed from it when the dilatometer is cooled (keeping $K_{\Delta v}$ and $K_{\Delta w}$ closed), which operates so as to cause a rise of the liquid meniscus in the stem, is of great importance when the question arises as to whether a maximum density can be shown to exist for helium or not. A second apparatus is therefore introduced having a very short stem and a similar capillary, but without a reservoir; to this the volumenometer W belongs. When the correction for the capillary of this control apparatus is calculated in exactly the same way as for the capillary of the dilatometer, it shows a rise of the level of the liquid that appears in the tube, and by comparing this with the observed rise one can obtain an indication of the accuracy of the correction.

For vapour density determinations the same dilatometer Δ_1 was used but along with the volumenometer Q; in this the gas was measured in a graduated tube, while it could be connected with Δ through $K_{\Delta Q}$ keeping $K_{\Delta r}$ closed.

§ 4. *Vapour Pressures of Helium.* The observed pressures have been corrected for the height of the helium surface above the middle of the thermometer reservoir $Th1'$, for the aerostatical pressure between the place where the pressure is measured and the surface of the liquid helium, and for the reduction of pressure due to friction along the coils of the regenerator spiral. In this way the following values were obtained:

Helium, maximum pressure.

Temperature			$760\ p_{coëx}$
I	II	mean.	
4°.29 K	4°.28 K	4°.29 K	760
3.97			565
3.26	3.20	3.23	197
2.34	2.40	2.37	51
1.47	1.49	1.48	3

Columns I and II refer to two independent measurements.

In fig. 1 of Pl. III $log.\ p \times 760$ (where p is expressed in atmospheres) is graphed as a function of $\frac{1}{T}$. At the same time the figure gives us an idea of the agreement with the VAN DER WAALS vapour pressure law $log.\ \frac{p}{p_k} = f\left(1 - \frac{T_k}{T}\right)$, from which it would follow that the curve should be a straight line.

The curvature of the experimental curve is but small, but it is still clear that f decreases at the lower temperatures.

If f is calculated from the tangent at $T = 4.^\circ 29$ K. it is found that $f = 1.2$, $T_k = 5.^\circ 8$ K., while the two temperatures 4.°29 and 3.°23 give $f = 1.1$, $T_k = 5.^\circ 7$ K. At lower temperatures f becomes still smaller, and the mean value would be found to be only $f = 0.9$, from which it would follow that $T_k = 6^{\circ}.4$, a value that considering the temperature of the BOYLE point, must certainly be too high.

It is worth remarking that this value of f differs very much from the values, ranging from 2 to 3, that have been found for ordinary normal substances [1]. Helium, then, shows in a greatly exaggerated form the deviation from the mean $f = 2.7$ for ordinary normal substances that is already noticeable in the case of substances whose critical temperature lies below 0° C. which give a value $f = 2.2$. Associative substances deviate in the opposite direction; for instance, for water $f = 3.26$ and for isobutyl alcohol $f = 4.17$.

The new light now thrown upon the vapour pressure law for helium also allows a new estimate of the lowest temperatures that were reached in the experiments published in the VAN BEMMELEN Jubilee book, which were then estimated upon a basis of $f = 2.2$. With the value now obtained, the temperature for a vapour pressure of 1 mm. should be 1°.33 K., and for 0.15 mm., which was the lowest pressure reached, the temperature should be 1°.15 K., while, to reach a temperature of 1° K., the vapour pressure would have to be lowered to 1/25 mm.

§ 5. *Densities of Liquid Helium.* In the following table containing the experimental results, densities are expressed in terms of the normal density of the gas.

From these values ϱ_{liq} is obtained by multiplying by $\varrho_{0^{\circ}C.\ 760\ mm.} = 0.0001787$, so that we now get $\varrho_{Liq.\ 4^{\circ}.29} = 0.122$, where the roughly approximate value 0.15 was given before.

The great decrease in the expansibility as the temperature is lowered is remarkable. In the experiments of 1909 described in Comm. N°. 112 the impression had already been created that this would prove to be the case; the density values then obtained are given in column I. The results are shown graphically in fig. 2, Pl. III, and it is particularly noteworthy that there seems to be a maximum in the density; from the figure this seems to be at about 2°.2 K. Furthermore, it was clearly observed that, when the temperature was being lowered and passed 2°.1 K., the meniscus in the stem of the dilatometer became stationary, and rose again as the temperature sank further to 1°.48 K., while the reverse phenomenon was observed as the temperature rose again from this point to 2°.37 K. The following

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[1] KUENEN, Zustandsgleichung p. 142.

Helium, liquid densities.

T	$\frac{1}{v_{A\,liq}}$			
	I	II	III	read-justed
4°.33 K	[658.0]			678.0
4°.29		682.3		682.3
4°.28			683.6	683.6
3°.98		715.5		715.5
3°.26		779.0		782.0
3°.20	784.8		785.9	785.9
2°.40	822.6		818.8	818.8
2°.34		815.4		820.0
1°.49			815.3	815.3
1°.47		810.9		815.0

results show that the meniscus really stands lower in the stem at 2°.37 K. than at 1°.48 K. and that this is not due to the influence of condensation of gas from the dilatometer stem

First experiment.

temperature		position of the meniscus	mean	
1°.47 K.			0.72	
2.34	before cooling	0.52		
	after cooling	0.49	0.505	
		difference	0.215	
		correction	0.06	difference 0.155

Second experiment.

temperature		position of the meniscus	mean	
1°.49 K.		0.59		
		0.58	0.587	
		0.59		
2°.40 K.		0.42		
		0.37	0.393	
		0.39		
	observed minimum	0.35		
		difference	0.194	
		correction	0.082	difference 0.112

An idea of the accuracy of the corrections applied in each case may be got from the fact that, in the second experiment, the control dilatometer showed a rise of the meniscus of 0.03 as the temperature fell, while the calculated value was 0.028. The mean number 0.134 that remains after the correction has been applied, must be ascribed to expansion between 2°.37 K. and 1°.48 K. As far as a conclusion could be drawn from the observation, a maximum density point for helium has to be accepted. From a single observation in which the vapour pressure of the bath was lowered to 1 mm. it would have followed that no further expansion occurs as the temperature is lowered still more; but, in the meantime, this one observation, during which the bath was not stirred, is too uncertain to allow a definite conclusion as to whether or not the density of helium after attaining a maximum decreases till it reaches an invariable value.

§ 5. *Vapour Densities of Helium.* The density at a pressure of 65.54 cm. and a temperature of 4°.29 K. was found to be 69.0 times the normal density. Calculating B from the equation $pv - RT = B/v$ we get $B = -0.000047$; and, for the density of the saturated vapour at a pressure of 76 cm. a value of 85.5 times the normal. The correction for C to be applied according to the mean reduced equation of state VII. 1, although undoubtedly appreciable, appears to be too uncertain. At 3°.23 K. by extrapolating values of the individual B's deduced from the helium isotherms between 0° and −216°.56 C. (Comm. N°. 102^a, Dec. 1907) B was found to be -0.000061, and this gives at 3°.23 K. a saturated vapour density 24.5 times the normal.

From these values various characteristic thermal data may be calculated for helium. If we deduce the slope of the MATHIAS diameter from 4°.29 K. and 3°.23 K. we find $-b_d = 0.0033$, and, taking the critical temperature to be 5°.5 K. and hence reaching the value $\varrho_{kd} = 0.065$, we get for the constant of the MATHIAS diameter $-\mathfrak{b}_d = 0.255$. MATHIAS foretold that the value of $-\mathfrak{b}_d$ would be small, and he suspected that it would be 0.14. The first part of his remarkable prophecy is, therefore, hereby fulfilled.

For the critical virial ratio $K_4 = \dfrac{RT_k}{p_k v_k}$ we get (taking $T_k = 5°.5$ K., and $p_k = 2.75$) from ϱ_{kd} a value 2.68, which is almost exactly the theoretical value deduced from the VAN DER WAALS equation of state. The value of this constant is thus markedly smaller for helium than for all other substances, with the exception of hydrogen, in which case it can be obtained only from very uncertain calculation yielding the result 2.9. (See KUENEN l. c. p. 60). The smallest known value is the one recently obtained for oxygen by E. MATHIAS and H. KAMERLINGH ONNES viz. 3.43. (Comm. N°. 117, March 1911). In a paper that will soon be published by C. A. CROMMELIN and H. KAMERLINGH ONNES[1]) a deduction from the isotherms of $K_4 = 3.28$ for argon will be given.

§ 6. *Molecular Attraction in Helium.* The occurrence of a maximum density in a substance of such simple constitution as helium gives rise to questions of great import from the point of view of molecular theory. With a substance like water it is easy to imagine a particular molecular combination by which some of the parts are more closely united, while others are separated, the whole leading to an increase of volume as the temperature is lowered, and this especially when one considers that the dielectric properties of water probably play a part in the phenomenon. But helium atoms we are forced to consider as spherical and smooth, and, as appears from the ZEEMAN-effect for helium, of the simplest possible internal construction; and for their case we seek in the meantime in vain for a basis for a similar explanation. Moreover, helium differs from ordinary normal substances, but in exactly the opposite way to that in which associated substances differ from them.

A dissociation increasing as the temperature is diminished, leading to an increase of the number of molecules (and, therefore of R in the equation of state), which would account for this deviation in the opposite sense, can scarcely be imagined. Should it appear that the change was occasioned by an increase in the dimensions of the helium atoms (that is, of b in the equation of state) as the temperature is lowered, then this, too, would be something strikingly unusual. The behaviour of helium seems rather to make it clear that even in the case of ordinary normal substances two different kinds of molecular attraction must be distinguished from each other — an attraction of comparatively large sphere of action, and an attraction that is local, but more intense, of smaller range, and confined to the immediate neighbourhood of the surface of the molecule; this latter attraction causes ordinary normal substances when compared with helium to resemble rather associative substances; in the case of liquid helium the latter type of action of the attraction would, then, be suppressed.

If it is not, indeed, entirely absent in helium, the sphere of influence of this force must have wholly withdrawn within the space occupied by the atom at the lowest temperatures (which is probably also to a large extent the case for substances like hydrogen at the

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[1]) Comm. N°. 120*a*, Proceedings of this Meeting p. 1012.

lowest temperatures at least); and, therefore, the predominance of characteristics which are just the reverse of those in associative substances leads to the supposition that in our case a part of the attraction diminishes with the temperature. Even this idea is at first sight strange, for we are familiar with the idea of attraction increasing as temperature falls. According to BOLTZMANN's law this increase must take place in a perfectly definite manner, even for a constant attraction between the molecules. When, therefore, we assume a decrease in the cohesion this must exist notwithstanding the cause for increase given by BOLTZMANN's law. It would, perhaps, be due to the fact, that at lower temperatures the decrease in the attractive force originating in the helium atom would predominate.

Let us work out a little further a modification that will affect the behaviour of the substance in such a way as to decrease the attraction, the a of VAN DER WAALS, with the temperature decreasing below a certain temperature. Its importance is far more radical than that which occasions an increase, for, while the latter changes the phenomenon more in degree, the former can occasion a fundamental alteration.

A few simple illustrations may illustrate this point. For the sake of simplicity let us take the VAN DER WAALS equation of state. Putting a and b constant for higher temperatures so that T_K can be calculated, and putting also the attraction $a = KT$ from $T = 0$ to $T = T_K$ and, therefore $a = KT_K$ at T_K, it follows then, in such a simple manner that it is not necessary to write down the equations here, that all temperatures below the critical T_k show the critical phenomena for $v = 3b$, the critical pressure being for every temperature proportional to the absolute temperature, viz. $\frac{1}{27}\frac{KT}{b^2}$. With respect to the individual isotherms, the gas above T_k behaves as a VAN DER WAALS substance, in correspondence with our assumption $a = const.$, but, for every temperature T below T_k, the isotherms are determined by taking the isotherm of T_k and shortening its ordinate in the ratio of T to T_k.

Assuming now that $a = KT$ holds only up to a certain temperature $T_1 < T_k$ and that $a = const.$ is the law from $T > T_1$ onwards, then the isotherms from the critical temperature to T_1 are determined from the equation of VAN DER WAALS, and from this equation, too, are determined the maximum vapour pressure, and liquid and vapour densities. Isotherms for lower temperatures are then determined from these by taking the ordinates for each volume from the isotherm for T_1 and diminishing it in ratio of T to T_1. The densities of coexisting liquid and vapour phases would thus remain unaltered, while their common pressure would be simply proportional to T. Although with helium the maximum vapour pressure diminishes less rapidly with the temperature than is the case with ordinary normal substances, the diminution is still very much greater in reality than would be the case under the conditions above assumed.

A substance that fulfilled these conditions would, moreover, exhibit some other very unusual properties. The energy change at constant temperature would be zero, the latent heat of vaporization would alone be necessary for external work, and so the internal latent heat of vaporization would be zero.

To realise the importance of the modifications which the thermodynamical properties of a substance undergo when the molecular attraction decreases with the temperature, let us assume that it decreases more rapidly than in simple ratio; in that case one is brought to the deduction of still stranger properties. We may here mention the case in which $a = cT^2$ for temperatures below $T_1 < T_k$. With such a substance at a temperature beneath T_1 lowering of the temperature would diminish the difference between the liquid and vapour densities, and this difference would disappear at a temperature T_{ki} determined from the conditions $\frac{dp}{dv} = 0$ and $\frac{d^2p}{dv^2} = 0$ by the equation $T_{ki}\ T_k = T_1^2$. Hence, an *inferior critical point* occurs from which to the absolute zero the substance once more behaves as a perfect gas. For this case the change of energy with volume is negative, and so too is, therefore, the internal latent heat.

We have still to examine if in other domains there are assumptions which are consistent with a decrease in the molecular attraction as the absolute zero is approached.

The nearest comes in this respect KELVIN's and J. J. THOMSON's idea of the structure of atoms. Assume, for example, that an atom consists of a sphere of uniformly distributed positive electricity inside which is an electron; then two such atoms would, at the absolute zero where the electron comes to rest, exert no electrical attraction upon each other. As soon, however, as the electrons begin to oscillate about their positions of equilibrium, and begin to describe orbits about their centres, attraction begins to be felt. An investigation similar to those made by VAN DER WAALS JR. based upon the principles of statistical mechanics would be necessary before one could say how the molecular attraction of a system of such atoms would depend upon the effects of collisions and of temperature radiation (they are, in fact, vibrators such as those assumed by PLANCK and

EINSTEIN). *A priori*, it seems to be not impossible that a increases over a definite temperature region as the temperature rises.

In the meantime all these theories do no more than emphasise the fact that the behaviour of helium forces us to question the significance of the absolute zero with respect to molecular attraction. Hence it is of first consequence to obtain data concerning the thermal properties here mentioned in connection with helium that would lead to the solution of these problems, and also to investigate related properties such as capillarity, viscosity, specific heat, refractive index and dielectric constant, for which data are still lacking. For this purpose the solution of the problem of transferring liquid helium to a vessel in which the regenerator spiral no longer interferes with the introduction of measuring apparatus is absolutely essential.

B. On the change in the resistance of pure metals at very low temperatures, etc.

III. The resistance of platinum at helium temperatures.

§ 1. *The resistance of a wire of very pure platinum at helium temperatures.* As soon as the possibility had been attained, it lay at hand to extend to helium temperatures the investigation of the change of electrical resistance of pure metals which, in Comm. N°. 99*c* (Sept. 1907), had been brought down to the lowest hydrogen temperatures. For this purpose the resistance Pt_B which had been calibrated at hydrogen temperatures as well as at others with the resistance Pt_I of Comm. N°. 99*b* (Sept. 1907) was available. It was constructed on the model of Pt_d (Comm. No. 99*b* § 2), and is indicated by Ω on Plate I of part *A* of the present paper, fig. 1. The thin platinum wire is wound round a glass cylinder and is kept tight on it by being wound while hot, and the thicker platinum ends W_a and W_b are fused to the glass. To these ends the double platinum leads W_{a_1}, W_{a_2} and W_{b_1}, W_{b_2} are attached; they are not, however, welded in the blowpipe, but are simply tin-soldered. The resistance was measured on the WEATSTONE bridge according to the method described in Comm. No. 99 and previous Communications. The ratios of w_t, the resistance at the temperature of the observation, to w_0, that at 0° C., are here given (p. 1108).

From this it appears that by descending to helium temperatures the resistance is still further diminished, but when these temperatures are reached the resistance attains a constant value quite independent of the individual temperature to which it has been brought. The

Resistance of platinum wire Pt_B

T	$\frac{W_t}{W_0}$
273°.09 K	1
20.2	0.0171
14.2	0.0135
4.3	0.0119
2.3	0.0119
1.5	0.0119

results are plotted in fig. 3 Pl. III, which shows well the asymptotical approach of the resistance to a constant value at 4°.3 K.

§ 2. *The probable resistance of pure platinum and of pure gold at helium temperatures.* In order to establish the exact significance of the result just obtained we must take account of the fact that the wire Pt_B was not made from quite pure metal, and we must allow for the probable influence of this difference from pure platinum.

With this end in view, we shall first confine our attention to the observations that have been made previously upon gold (Comm. N°. 99^c). Remembering the close resemblance between the differences of the resistances of platinum and of gold wires from a linear function of the temperature, we may, in view of the result that has been obtained with platinum, extrapolate the Au_V-resistance curve to give a constant value at helium temperatures. This has been done in fig. 3 of Plate III. The parts of the curves obtained from observations are drawn with thicker lines. We now note that, according to § 1 of Comm. N°. 99c by KAMERLINGH ONNES and CLAY (Sept. 1907) the influence of admixtures can be represented with rough approximation even down to hydrogen temperatures by an additive resistance that is independent of the temperature. In this way the line correspondingly marked in the figure was obtained for Au_{III} which was constructed of gold of a smaller degree of purity (0.015°/₀ admixture against 0.005°/₀ for Au_V). According, now, to § 1 of Comm. N°. 99c the effect of admixture should be pretty well proportional to the quantity present, and this would lead to negative values for pure gold. In the first place, however, we do not know if the impurity was the same in the two cases, nor do we know the influence of possible tensions in the metal; but moreover, such great uncertainty exists in our rough approximations as to confine our most probable result in the meantime to this: That within the limits of experimental error (the degree of purity attainable) the resistance of pure gold is already zero at helium temperatures.

Let us return to platinum. The wire Pt_B seems to be less pure than Pt_I (see table V of Comm. N°. 99*b*), and, moreover, the fixing of the wire on the glass may give rise to undesirable effects. By putting the additive resistance once more constant, to a first approximation, extrapolation gives for Pt_I the corresponding line shown in the graph. But still, the resistance of Pt_I may not without further comment be regarded as the resistance of pure platinum. A wire of greater diameter used by HOLBORN gave a greater relative decrease of the resistance from 0° to — 191° C. If we extrapolate these values to lower temperatures the resistance remaining at helium temperatures, and independent of any further change of temperature, would be nearer zero. One may ask if it is not possible to put the difference between the two wires obtained from HERAEUS inversely proportional to the thickness and in that way deduce a value for pure platinum unaffected by the individual treatment of each; but this method would lead us too far into the region of pure conjecture. But still, the conclusion seems to be fully established that the resistance of pure platinum is, within the limits of experimental error — the attainable degree of purity — already zero at helium temperatures.

§ 3. *The change with temperature of the resistance of pure metals at low temperatures.* I was formerly of the opinion that the resistance of pure metals reaches a minimum as the temperature is diminished, and then, as the temperature sinks still further, again begins to increase and becomes infinitely great at the absolute zero; but now it seems to me to be more probable that, even before the absolute zero is actually reached, the resistance if not zero, has become so extremely small that it practically vanishes, and that this remains the case for further lowering of the temperature.

In view of this result, then, we must also abandon the theory that has served for years as a guide in our Leiden researches upon the resistance of metals at low temperatures, according to which it was imagined that the resistance would attain a minimum as the temperature was lowered and would become infinitely great at $T = 0$, in consequence of the assumption that the electrons which are the actual conductors in metals would, as was expressed by me in 1904, begin to precipitate on the atoms as a vapour on being cooled to hydrogen temperatures, or as Koenigsberger — in a manner leading to a similar dependence upon temperature — explains the phenomenon that was then supposed to exist, by the recombination of the electrons that had been freed by dissociation. I already questioned the validity of this assumption with respect to its application to perfectly pure metals at hydrogen temperatures, when the latest experimental results (Comm. by Kamerlingh Onnes and Clay) obtained with extremely pure gold showed that the point of proportionality would always have to be sought at still lower temperatures. It is now quite clear that in the case of metals like gold and platinum at any rate that theory must be dropped. It seems that the free electrons in the main remain free, and it seems to be the movable parts of the vibrators that are now bound, their motion at ordinary temperature forming the obstacles to conduction; these disappear when the temperature is lowered sufficiently as the vibrators become then practically immovable [1]). There is, in the meantime, no occasion to calculate, unless for still much lower temperatures which cannot just yet be realised, a "latent heat of vaporization" or a "dissociation constant" for the electrons for the case of pure metals of the type treated.

The marked decrease in the resistance until it becomes practically zero at a temperature just above 4° K. and its remaining at this value as the temperature is lowered further as has been shown over a range of about two and a half degrees, so that, as far as resistance of these metals is concerned, the boiling point of helium is practically the absolute zero, points in another direction. It seems to me to be connected with the change with temperature of the heat energy of molecular motion of solid substances that has been deduced by Einstein in his theory of the specific heats, on the assumption that it is the energy of vibrators determined by radiation equilibrium.

In particular an obvious assumption to make is that the mean free path of the electrons which provide conduction is determined by the elongation of the above mentioned vibrators. To further illustrate this point let us keep as closely as possible to the theory of electrical resistance of Riecke [2]), Drude and Lorentz, who has developed it into a pure theory of electrons. We take the formula

$$\gamma = \frac{1}{3}\frac{\varepsilon^2}{c^2}\frac{NLg}{aT}$$

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[1]) That the vibrators become practically immovable represents what we have formerly called the "freezing" of the electrons.

[2]) Riecke, Physik. ZS. 1909, p. 512

where γ is the electrical conductivity of a cube of unit volume, N the density of the free electrons, L their mean free path, $\mathfrak{g}$ their molecular speed, and c the speed of light, ε the elementary charge and αT the kinetic energy of a free electron while T is the absolute temperature. Putting $p=\frac{1}{3}\frac{\varepsilon^2}{c^2}\frac{\mathfrak{g}}{\alpha\sqrt{T}}$, this becomes

$$\gamma=\frac{pNL}{\sqrt{T}}$$

and according to RIECKE if $q=\frac{a\sqrt{T_s}}{\pi(1+\beta s)^2}$, where a is the distance between the atoms supposed to be cubically arranged, s the ordinary and T_s the absolute temperature of the melting point, β in RIECKE's notation the coefficient of linear expansion, $L=\frac{q}{\sqrt{T}}$. Instead of this hypothesis of RIECKE's we shall put

$$L=\frac{q}{\sqrt{E_T}}$$

in which

$$E_T=3R\frac{\beta r}{e^{\frac{\beta r}{T}}-1}$$

where $\beta=4.864.10^{-11}$, now represents, according to PLANCK, the energy of a vibrator whose frequency is r. The product βr we will call as usually is done a.

We then get for the ratio of the conductivity γ_T at any temperature T, to γ_0 that at 0° C. the value:

$$\frac{\gamma_T}{\gamma_0}=\frac{\sqrt{T_{0^\circ C}\,.E_{0^\circ C}}}{\sqrt{TE_T}}\ .$$

This formula gives, in fact, good expression to the decrease with temperature of the resistance of pure metals of the kind here considered (monatomic [2]). It shows in the first place the decrease to zero at a temperature above the absolute zero. For $\beta r=a=54$ the resistance at helium temperatures becomes about 0.0001 times that at 0°C.

If we may further assume that $\frac{a}{T}$ is already small at 0° C., then the resistance w_T at T in terms of the resistance w_0 at 0° C. becomes

$$\frac{w_T}{w_0}=\frac{T-\frac{1}{4}a}{273.1-\frac{1}{4}a}\ .$$

In fact, at 0°C. the temperature coefficients of the resistances of pure metals are, as a rule, greater than 0.00367, and, for platinum, gold, silver and lead they lie in the neighbourhood of 0.0039 and 0.0040.

And lastly, the formula also expresses well the fact that the diminution of resistance diminishes in quantity at hydrogen temperatures, and that in greater degree for substances of high melting point than for those of low melting point.

An accurate numerical equation, however, such as to determine even the bend in the curve that represents the resistance as a function of the temperature can be obtained only on the assumption that smaller values of ν and, therefore, of a come in the front at lower temperatures. Definite values, indeed, cannot be ascribed to ν. EINSTEIN[1]), for instance, deduces from its elasticity $a = 200$ for silver (for he gives $\lambda = 73.10^{-4}$ cm. for the wave-length in vacuum corresponding to ν), while NERNST[2]) from the specific heat, deduces the value $a = 162$ corresponding to $\lambda = 90.10^{-4}$, a number, however, which is not of itself sufficient to represent the whole behaviour of silver. For lead, NERNST gives $a = 58$, while EINSTEIN gets $a = 104$ from the elasticity. Moreover according to the elasticity a should increase somewhat at lower temperatures, while from the specific heat, it would appear that the change should take place in the same sense as that in which the resistance changes This, too, shows that the theory is still far from perfect.

As there exists so much uncertainty, and as it is more a question of showing that the introduction of vibrators leads to a qualitative explanation of the sense in which the observed change of resistance deviates from proportionality to temperature, I have taken for a one half of each of the values obtained by EINSTEIN from the elasticity. In this way we obtain for a:

for Pt 111, Ag 100, Au 92, Pb 54.

It appears, therefore, that there is indeed a qualitative correspondence[3]). Before we can attach any greater importance to it, howe-

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[1]) A. EINSTEIN Ann. d. Phys. (4) 34 (1911) p. 170. Since the address delivered in the December meeting was only ready for printing in the number of the Dutch Proceedings for February 1911, I have been able to add then the following calculations from the elasticity to what I communicated in December.

[2]) Cf. also MADELUNG, Gött. Nachr. 1909, p. 100, who was the first to calculate the period of molecular vibrations.

[3]) The numbers are all taken from the Leiden observations (KAMERLINGH ONNES and CLAY l. c.) and they refer to the purest of the wires, while the probable negative correction for the influence of admixture and for the results of treatment during manufacture necessary for its expression in terms of the pure metal have

$$\frac{W_T}{W_0}$$

T	$\frac{T}{273.1}$	platinum		silver		gold		lead	
		C	O	C	O	C	O	C	O
379°86	1 365	1.405		1.401	1.411	1 397		1.384	
273.1	1.	1.	1.	1.	1.	1.	1.	1.	1.
169.29	0.617	0.579	0.581	0 583	0.581	0.586	0.593	0.601	0.594
77.93	0.285	0 213	0.199	0.220	0.197	0.225	0.219	0.250	0.253
20.18	0.074	0.012	0.014	0.015	0.009	0.018	0 008	0.035	0.030
13.88	0.054	0.003	0.010	0.004	0 007	0.005	0.003	0.015	0.012
4.30	0.016	0.000	[0 009]	0.000		0.000	[0.002]	0.000	

ver, it would have to be shown that the ratio of heat conductivity to electrical conductivity at hydrogen temperatures [1]) satisfies the conditions imposed by RIECKE's modified theory [2]).

At all events in developing new theoretical considerations it seems desirable to take into account the result obtained [3]).

I gratefully record my indebtedness to Dr. C. DORSMAN for his intelligent assistance during the whole of this investigation, and to Mr. G. HOLST, who conducted the measurements with the WHEATSTONE-bridge with much care.

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been omitted. The influence of admixture is such as to give rise to impediments distributed, at distances determined by the quantity of admixture present, throughout the metal, which exert an influence upon the mean free path of the free electrons, that is proportional to $1/T$ and therefore an influence on the resistance that is independent of the temperature just as mixed crystals do in alloys.

Estimating for mercury $a = 30$ on account of its lower melting point, we get the following multiples of the value extrapolated to 0° C. from observations on the solid state (loc. cit.).

T	77°,29 K.	20°,8 K.	13°,88 K.
calculated	0,263	0,050	0,027
observed	0,264	0,056	0,033

[1]) Experiments to elucidate this point have been in preparation for some time.

[2]) An assumption that may obviously be made is that the energy of the vibrators determines the increase of volume from the absolute zero, with which the explanation of the relation between expansion and change of resistance on one hand, and between expansion coefficient and specific heat on the other hand, deserves to find a place in the theory.

[3]) The further question calls for attention that is suggested by it regarding the peculiarities of the motion of electrons through conductors when, by taking all precautions, the mean free paths are as large as must, in the meantime, be assumed that they can be made (and begin to be comparable with the thickness of very thin layers).

Physics. — "*Ionization of gases by light, emitted from* GEISSLER *tubes. Research after the existence of selective effects in the ionization.*" By H. G. CANNEGIETER. (Communicated by Prof. W. H. JULIUS).

Since HALLWACHS' [1]) discovery that an insulated, negatively charged zincplate loses its charge, when ultra-violet light falls upon it, this property of the ultraviolet light has been a subject of research to many observers. Several solids and liquids prove photoelectric, i.e. when exposed to the light they send out negatively charged particles, whereas they acquire a positive charge themselves, if they were uncharged at first.

On gases too the ultra-violet light has an influence. When the light shines through them, they acquire conductivity; the light ionizes the gasmolecules.

If we put the question, how we are to figure the action of the ether-vibrations on the molecules of substances, which led to the loosening of negatively charged particles from them, we are inclined to take it for an effect of resonance. If the molecules of the substance, solid, liquid or gas, on which the light is shining are struck by vibrations, the period of which corresponds to those which the electrons in the molecules can emit themselves under certain circumstances, then the electrons will by resonance get so strong a motion, that they are loosened from the molecule and will behave like free particles.

From this point of view we may expect that, if a given substance in the luminous state emits electrically acting rays, this same substance, when struck by these particular rays, will be more photoelectric, than when it is under the influence of rays from any other source of light; also we may take for granted that, examining the effect of the radiation, emitted from the above mentioned source of light, on different substances, including the substance emitting the active rays, the effect on this latter substance, when compared to that on the other substances under examination, will be found the strongest.

If we use as sources of light discharge tubes filled with different gases, and examine the ionization excited by the light in the same gases, then it will be possible for us to arrange them in a definite order, according to the measured effect, which order will depend

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[1]) Wied. Ann. **33**, 301, 1888.

on the source of light we have used. It may be expected, that when the ionisationroom contains the same gas which fills the discharge tube, this gas will be more influenced by the ionizing rays than any other.

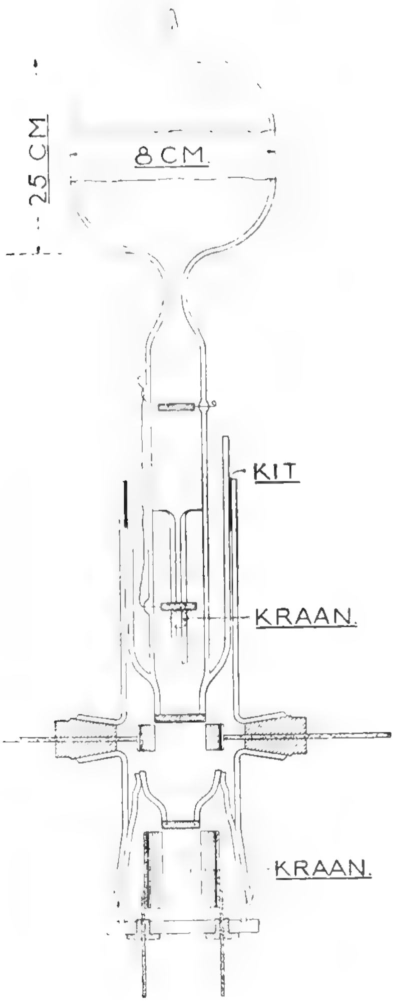
In the following pages a short account will be given of a research after the existence of similar selective effects in the ionization of gases under the influence of light emitted by Geissler tubes. For particulars we refer to a dissertation which is to appear within a few weeks.

Three methods may be followed in order to find out whether ions are formed in a gas by radiation. Firstly we can show the existence of ions in damp gas by condensing the aqueous vapour on them. Secondly we can make the gas pass along a charged conductor or through a condensator after it has been struck by the ionizing rays; if the gas has got conductivity the conductor or the condensator will be discharged. And in the third place, if the gas under examination is at rest between the plates of a condensator or in the neighbourhood of a charged conductor, then there will be a current in the condensator, or the conductor will lose its charge, when the radiation has caused ionization.

In using the former two methods the risk of erroneous results by photoelectric action on minute drops of water or floating dust particles is greater than in using the third; therefore the latter method was chosen for the research described here. Moreover it makes it possible for us to measure the ionization at different pressures in the gas under examination.

The apparatus used for the experiments was made of glass and consisted of three separate partitions, viz. the discharge tube, the absorptionroom and the ionizationroom. Composed in this way it gave an opportunity for examining the absorption of different gases for the ionizing rays and so made it possible for us to study an eventual connection between ionization and absorption, besides to find out the possible existence of selective effects in the absorption also.

The ionizationroom, or condensatorroom, forms a separate part of the apparatus. It is closed on one end by a ground-in basin-shaped piece of glass, the bottom of which is a fluorite plate of 15 m.M. diameter and 3 m.M. thickness. On the other side a glass plate is cemented against the ground edge. In this plate are two holes, shut by amber plugs cemented into them, which are at the same



time the bearers of the condensatorplates. The wall of the condensatorroom, ground at the outside, forms the cone of a groundin joint, the neck of which is the end of a cylindrical tube forming the principal part of the apparatus. On this neck is made a stop-cock; in the wall of the condensatorroom there is a little hole, which can be placed opposite the stop-cock. In this way we can exhaust the room between the condensatorplates and fill it with the different gases under research.

In the other, straight end of the above mentioned cylindrical tube the discharge tube is cemented in. The open space between the discharge tube and the ionizationroom forms the absorptionroom. By means of a stop-cock this room too can be exhausted and filled with other gases.

The discharge tube was made in the way described by LYMAN[1]), with internal capillary and ringshaped aluminium electrodes. It was closed by a fluorite window, 20 m.M. diameter, 3 m.M. thick, and provided with a glass mantle fitting in the cylindrical tube of the apparatus. A pair of electrodes in the absorptionroom were not fit for use because of photoelectric effects presenting themselves.

The arrangement of the apparatus insures perfect air-tightness of both ionization and absorptionroom. The distance between the fluorite windows of the discharge tube and the ionizationroom was regulated in such a way that no rays from the discharge tube could strike the plates of the condensator, in order to prevent mistakes by photoelectric effects on the electrodes in the ionizationroom.

As during the examination no changes may take place in the

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[1]) Astrophys. J 19, 181, 1906.

discharge tube, the fact that many gases in the discharge tube combine with the metal of the electrodes under the influence of the discharges, or, if they are compounds, break up into their components, is the reason that only a limited number of gases are fit for a research as is here described.

Therefore hydrogen and oxygen are chosen for our research; we have also tried to get comparable results with carbon monoxide, notwithstanding the peculiarity of this gas to vanish in the discharge tube by the beforesaid reason.

In order to diminish as much as possible the troubles caused by this process, the discharge tube was provided with a reservoir measuring ten times the tube itself. A copper box could be put around the reservoir; by heating this box with a heating spiral the gas in the reservoir could be heated, and so the pressure in the gas could be increased, if it had decreased by the selfexhausting process.

We studied the ionization by radiation with the three sources of light in the same three gases and besides in air and oxygen. The absorption was examined as well, and also the way in which effect and absorption change, if the pressure in the gas is lowered.

The measurements were made with a CREMER—EDELMANN string-electrometer.

One of the plates of the condensator was kept on a constant potential varying from 20 tot 320 Volts, the other was connected with the electrometer. The system condensatorplate + electrometer was put to earth; the earth connection could be broken quickly by a special device. If under the influence of the radiation the gas gets conductivity, the insulated plate begins to charge itself. The rapidity with which this happened gave the rate of the conductivity in the gas. The time the system needed to charge itself to a certain potential was measured with a stopwatch.

The capacity of the system condensatorplate + electrometer was 18 c.M. A rapidity of charge of 1 Volt per sec. corresponded with a current of 20×10^{-12} Amp. in the condensator. The exactitude reached in the measuring was 5 %.

The expectation that the research would show selective effects in the ionization of gases has not come true. The effect caused by the hydrogen radiation as well as by the nitrogen and carbon monoxide-radiation proved dependent on the pressure of the gas; whereas the mutual proportion of the effect on the different gases was found to vary with the pressure in the gas. The value of this mutual proportion

Proport. of the measured effect	$\frac{H_2}{CO}$	$\frac{H_2}{N_2}$	$\frac{CO}{H_2}$	$\frac{CO}{N_2}$	$\frac{N_2}{H_2}$	$\frac{N_2}{CO}$	$\frac{H_2}{air}$	$\frac{H_2}{O_2}$	Absolute value of the effect on hydrogen
caused by	RADIATION OF HYDROGEN, PRESSURE IN THE TUBE 1.2 mm.								
at 500 mm.	**1.17**	**1.17**	0.855	1.00	0.855	1.00	6.90	55.20	3.1×10^{-12} Amp.
400 „	**1.46**	**1.46**	0.685	1.00	0.685	1.00	5.23	47.64	4.3×10^{-10} „
300 „	**1.66**	**1.66**	0.603	1.00	0.60	1.00	4.37	44.10	5.6×10^{-12} „
200 „	**1.60**	**1.60**	0.625	1.00	0.625	1.00	3.99	33.30	6.9×10^{-12} „
100 „	**1.21**	**1.21**	0.826	1.00	0.826	1.00	4.05	24.90	8.5×10^{-12} „
20 „	**0.77**	**0.77**	1.30	1.00	1.30	1.00	2.00	8.70	10.8×10^{-12} „
10 „	**0.75**	**0.80**	1.33	0.971	1.25	1.63	1.63	4.55	11.4×10^{-12} „
1.0 „	**0.82**	**0.60**	1.21	0.73	1.67	1.36	0.78	2.01	13.6×10^{-12} „
low [1]	**0.94**	**0.52**	1.06	0.530	1.92	1.89	0.68	0.97	16.0×10^{-12} „
caused by	RADIATION OF HYDROGEN, PRESSURE IN THE TUBE 1.0 mm.								
at 500 mm.	**7.93**	**23.80**	0.126	3.00	0.042	0.333	—	—	0.71×10^{-12} Amp.
400 „	**4.00**	**17.33**	0.250	4.33	0.058	0.231	—	—	0.78×10^{-12} „
300 „	**2.82**	**14.10**	0.355	5.00	0.071	0.200	-	—	0.85×10^{-12} „
200 „	**2.30**	**12.40**	0.435	5.40	0.081	0.185	—	—	0.93×10^{-12} „
100 „	**2.06**	**5.25**	0.485	2.55	0.191	0.392	—	—	1.05×10^{-12} „
20 „	**1.54**	**2.59**	0.649	1.68	0.386	0.596	4.1	16.5	1.32×10^{-12} „
10 „	**1.49**	**1.84**	0.671	1.23	0.543	0.813	3.4	15.0	1.35×10^{-12} „
1.0 „	**1.56**	**1.95**	0.641	1.25	0.513	0.800	2.4	2.1	1.95×10^{-12} „
low	**1.07**	**1.29**	0.938	1.21	0.774	0.834	1.0	1.0	2.40×10^{-12} „
caused by	RADIATION OF CARBON MONOXIDE.								
at 500 mm.	1.30	52.00	**0.77**	**40.00**	0.019	0.025	—	—	0.456×10^{-12} Amp.
400 „	1.30	22.50	**0.76**	**17.00**	0.045	0.59	—	—	0.225×10^{-12} „
300 „	1.39	8.31	**0.72**	**6.00**	0.420	0.17	—	—	0.291×10^{-12} „
200 „	1.39	5.52	**0.72**	**4.00**	0.181	0.25	—	—	0.348×10^{-12} „
100 „	1.32	3.33	**0.76**	**2.54**	0.301	0.394	8.00	—	0.420×10^{-12} „
20 „	1.21	1.90	**0.83**	**1.58**	0.526	0.632	2.52	22.50	0.540×10^{-12} „
10 „	1.15	1.56	**0.87**	**1.38**	0.641	0.724	1.84	11.59	0.585×10^{-12} „
1.0 „	1.33	1.40	**0.75**	**1.05**	0.714	0.952	0.77	4.84	0.800×10^{-12} „
low	1.28	1.67	**0.78**	**1.30**	0.598	0.769	0.60	1.73	1.000×10^{-12} „
caused by	RADIATION OF NITROGEN.								
at 500 mm.		—		—	—	-	·	—	—
300 „	—	—	—	—	—	—	·	—	—
100 „	—	—	—	—	—	—	—	—	—
50 „	1.35	2.13	0.741	1.60	**0.47**	**0.625**	-	—	0.054×10^{-12} Amp.
20 „	1.47	1.82	0.681	1.25	**0.55**	**0.800**	—	—	0.066×10^{-12} „
10 „	1.44	1.64	0.695	1.14	**0.61**	**0.875**		—	0.069×10^{-12} „
5 „	1.41	1.49	0.710	1.06	**0.67**	**0.941**	—	—	0.072×10^{-12} „
1.0 „	0.98	0.89	1.02	0.90	**1.13**	**1.11**		—	0.090×10^{-12} „
low	0.66	0.87	1.51	1.33	**1.15**	**0.754**	-	—	0.120×10^{-12} „

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[1] "Low" means here that the pressure in the condensatorroom was less than 0.1 mm.

under different circumstances is given in the additional table. This table shows that, when the pressure is high, the ionization is always strongest in hydrogen, and after that in carbon monoxide, nitrogen, air, oxygen. If the pressure in the gas under examination is lowered, the proportion changes. Concerning this change may be said that the curve representing its character shows in all gases an ascent, slow under high pressures and sharper under lower ones. Under very low pressures a slight decrease of pressure shows a considerable increase of the effect.

The table mentions the results of the observations made with two hydrogen tubes filled at different pressures; further with a carbon monoxide, and a nitrogen tube. The first, second, and third columns refer to the proportion between the effect measured resp. on hydrogen, carbon monoxide and nitrogen, and the effect observed in the two other gases the radiation of which has been examined. The fourth column gives the proportion between the effect on hydrogen and that on air and oxygen. In column N°. 5 are given the absolute values of the currents measured in hydrogen. The character and the rapidity of the increase of the effect with decrease of the pressure in the gas may be judged therefrom. The numbers are interpolated; they do not refer to observations made at just the given pressure. The conditions in the absorptionroom were always alike; the pressure in it was always so low that the active rays were not absorbed.

ERRATA.

In the Proceedings of the Meeting of March 25, 1911:

p. 942 line 17 from the top read: *Method. First Part. The Densimeter.*

,, 946 ,, 7 ,, ,, bottom ,, : *Method. Second Part. The Volumenometer.*

,, 948 ,, 15 ,, ,, ,, : for "In this we", read: "We".

,, 949 ,, 12 ,, ,, top : for *Experimental method,* read: *Course of the experiments.*

(April 20, 1911).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Friday April 28, 1911.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Vrijdag 28 April 1911, Dl. XIX).

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J. G. Dusser de Barenne: "The action of strychnine on the central nervous system. The segmental, strictly localized strychnine-intoxication of the dorsal spinal mechanisms: a contribution to the dermatomery of the hind leg in dogs". (Communicated by Prof. C. Winkler), p. 1146.

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H. Kamerlingh Onnes: "Further experiments with liquid helium. C. On the change of electric resistance of pure metals at very low temperatures etc. IV. The resistance of pure mercury at helium temperatures", p. 1274.

Errata, p. 1276.

Geology. — *"On Orbitoides in the neighbourhood of the Balik Papan Bay, East-coast of Borneo."* By L. RUTTEN. (Communicated by Prof. A. WICHMANN).

(Communicated in the meeting of February 25, 1911).

During a four months' exploration near the Balik-Papan Bay executed by order of the "Nederlandsche Maatschappij tot het verrichten van Mijnbouwkundige Werken", the general geological results of which are described elsewhere, I collected rocks containing Foraminifera in several places.

With the consent of the Director of the Department of Agriculture, Mr. LOVINK I could make a thorough study of part of these fossils in the laboratory for geological observations at Buitenzorg, where the superintendent Dr. J. MOHR, with the greatest affability, set a room apart for me and was constantly ready to lend me a helping hand during the investigation.

I regret I had to dispose neither of sufficient time, nor of sufficient literature to be able to determine all Foraminifera; the greater part of the work was devoted to the Orbitoides which occurred in different species and a great number of specimens among my material. Together with the description of the Orbitoides, likewise the other Foraminifera will be mentioned, in so far as they could be determined.

For orientation a sketch-map on a scale of 1.250.000 is added to this communication, on which the places where the fossils have been found, are indicated, the principal ones by crosses, the others by circlets. Whereas Foraminifera occur chiefly in pure limestone or in hard marl, in which they can only be seen distinctly in thin sections, I succeeded in finding looser marl, from which the Foraminifera could be washed out in great quantities. The first place lies on the Sungei (river) Palamuan, about 2 km. west of the kampong of that name, the second on the Sungei Blakin, the last on the upper-course of the Sungei Mentawir. These three places are indicated on the map by a cross. Of these three places the one on the Sungei Pamaluan is the oldest, that on the Sungei Mentawir the youngest. The greater part of the Foraminifera collected at these spots is in the collection of the Mineralogical-Geological Institute of the University of Utrecht; during my investigation I only disposed of small specimens which I had left behind here, so that it is not impossible that the chief material contains still some other forms than those I am about to describe.

The greater part of the forms I am going to describe, come from the three places mentioned; I found only one species in a limestone at the declivity of the mountain-range where is the source of the Sungei Sepaku, which is as old as the strata on the Sungei Pamaluan; Orbitoides were likewise found in marl in Pulu Balan, on the Sungei Binuwang, and in the delta of the Sungei Pamaluan, but these were not distinct enough to allow a specific determination.

As all Orbitoides found belong to the subgenus Lepidocyclina and to the still younger, new subgenus Lepidosemicyclina, all strata are of a posteocene age [1]).

A very great number of sorts of Lepidocyclina of the Indian Archipelago has already been described; I shall try to group these species in such a way as to give an easy survey of them, I am however quite aware of the fact that most likely I shall not fully succeed in this respect, on account of insufficient knowledge of the literature and inaccessibility of a great number of publications which, though not directly relating to the Indian forms, are nevertheless of great importance for the knowledge of Orbitoides.

Among the Lepidocyclina known in India some are easily distinguished because they are not round but star-shaped and even polygonal; one form is characterized by the appearance of several strata of median chambers, whilst both, the very large and the very small ones, can be easily separated from the others. The greatest difficulties offer the species with normal forms and average sizes.

If in this communication numbers are given about the dimensions of Orbitoides *d* always means the horizontal diameter, *h* the height (thickness).

1. Species of polygonal or radial form. To these belong *O. radiata* MARTIN [2]) *O. Martini* SCHLUMBERGER [3]), both of Java and perhaps *O. murrayana* JONES and CHAPMAN [4]), of Christmas Island. O. radiata has an undulated circumference, the diameter is 8 m.m., O. Martini is purely star-shaped, the maximum-diameter is 6 m.m., O. murrayana, of which only a horizontal section is known, is quadrangular; *d* is 9,375 m.m. DOUVILLÉ has however rightly pointed out [5]) that the latter form is perhaps not star-shaped or polygonal at all, but round and bent strongly saddle-shaped, so that the horizontal section must obtain a polygonal or star-shaped figure.

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[1]) K. MARTIN, Samml. d. Geol. Reichsmuseums of Leiden, 6. p. 132—245, 1902.

[2]) K. MARTIN, Die Tertiärschichten auf Java. 1880.

[3]) C. SCHLUMBERGER, Samml d. Geol. Reichsmuseums in Leiden, 6, p. 128—134. 1901.

[4]) T. RUPERT JONES and F. CHAPMAM, On the Foraminifera of the Orbitoidal Limestone and Reef Rocks of Christmas Island, in: C. ANDREWS, A Monograph Christmas Island, 1900, p. 226—264.

[5]) H. DOUVILLÉ, Bull. Soc. Géol. de France (4) 5, p. 435—465. 1905.

2. Species with more than 1 stratum of median chambers. As a form of this nature has only been described *O. multipartita* MARTIN[1]). The median chambers occur only in more than 1 stratum at the periphery, where the lateral chambers are reduced; *d* is about 7 mm. Only the form found in Java has been described. It is however my opinion that two forms of Christmas Island described by JONES and CHAPMAN (l.c.), i.e. *O. insulae natalis var. inaequali* and *O. ephippoides* should likewise be classed among O. multipartita. In the former one distinctly sees in the representation several strata of median chambers at the periphery, whilst the embryonal ventricle is large, as with O. multipartita. For the rest DOUVILLÉ has pointed out already that there was no reason for the introduction of a new species: O. ephippoides (l.c.).

3. Small species. The oldest description known of these is *O. Sumatrensis* BRADY [2]), which is nearly globe-shaped, *d* 3, *h* $1\frac{1}{2}$—$\frac{1}{2}$ mm. The median plane forms at the periphery a thin keel; only small macrospheric forms are known [3]) with certainty; of the microspheric forms it is only occasionally mentioned that they can reach 15 m.m. diameter [4]). Nias [2]), Sarawak [3]), S. Borneo [4]) and Christmas Island [5]).

K. MARTIN [6]) has described a very small form of Timor but not given it a name, which seems in the main to be similar to O. Sumatrensis BRADY, in the middle the scale becomes gradually thicker, and the embryonal chamber and the succeeding one are very large, the Timor-form is only somewhat smaller and less globular: *d* 1—2, *h* 1—$\frac{1}{2}$ mm. Timor (GUNUNG ILHAUW), S. Borneo [7]) New Guinea [8]).

Another, very small form of Timor [6]), however, differs decidedly from O. Sumatrensis by its flattening. For convenience' sake we shall indicate it as *O. Timor* 1.

Somewhat larger is a form described by BRADY [2]) as O. dispansa; afterwards VERBEEK and FENNEMA [9]) proved this determination to be

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[1]) K. MARTIN, Die Fossilien von Java, Erstes Heft. 1891.

[2]) H. BRADY, Jaarb. v. h. Mijnwezen in Ned. Indië, 7, p. 157—169, 1878.

[3]) R. BULLEN NEWTON and R. HOLLAND, The Ann. and Magazine of Natural History (7). 3, p. 245—264, 1899.

[4]) H. DOUVILLÉ, l.c.

[5]) T. RUPERT JONES and F. CHAPMAN, l.c.

[6]) K. MARTIN, Samml. des Geol. Reichsmuseums in Leiden, 1, p. 1—64, 1881.

[7]) K. MARTIN, Samml. des Geol. Reichsmuseums in Leiden, 1, p. 131—193, 1883.

[8]) K. MARTIN, Samml. des Geol. Reichsmuseums in Leiden, 1, p. 65—83.

[9]) R. VERBEEK et R. FENNEMA, Description géol. de Java et Madura, p. 1176—1182, 1896.

incorrect, and determined it as their O. 1A. *d* 6, *h* 2 mm. The disk is in the centrum gradually thickened, and on both sides covered with warts (on BRADY's representation I count about 40 of these). Afterwards as a new sort of Christmas Island *O. neodispansa* has been described by JONES and CHAPMAM [1]), the diagnosis of which O. dispansa BRADY and O. 1A VERBEEK and FENNEMA (*d* 5, *h* 1½ mm.) This O. neodispansa consequently seems to occur in Christmas Island [1]), Nias [1]), Padangsche Bovenlanden [1]) and Java.

At all events *O.* 2*C* and *O.* 2*D* VERBEEK and FENNEMA [1]) differ from this O. neodispansa, the former of which is megalospheric, the latter microspheric, according to the representation the scale is quite smooth and provided with a central tubercle, *d* 5—6 *h* 2 mm. Java.

At last the megalospheric form of *O Tournoueri* LEM. et DOUVILLÉ (*d* 4—5 mm.) which has only a few warts in the centrum, belongs to these small forms. [1]).

4. Large Forms. A great many large Orbitoides from the Indian Archipelago have been described, which, as they are not yet completely known, can be determined either with great difficulty or not at all. To these belong *O. gigantea* MARTIN [1]), *O. Carteri* MARTIN [2]), *O.* 3 *E* and *O.* 3 *F* VERBEEK and FENNEMA [1]), all of Java. Of the latter two, the former is again micro- the other megalospheric. Most likely a few more are hidden among these two sorts, as for their horizontal diameter is given 4⅓—70 mm., which is certainly a too great variability. A common property is the spatulate form of the median chambers, on horizontal section and their large dimensions (max. 0.250 mm. radial with 0.2000 mm. tangential), which is much more than with the evidently allied O. Mantelli.

Another gigantic incompletely known Orbitoid which consequently did not receive a name, is found in Great-Kei (*d* 70 mm.) [1]). Two large, incompletely known forms are found in Timor [1]), one of these has median chambers as O. Mantelli Mort [3]).

A pretty large Orbitoid of Christmas Island *O. insulae-natalis* was first, very incompletely, and only on account of the vertical

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[1]) Vide previous page.

[2]) K. MARTIN. Die Tertiairschichten auf Java 1880.

[3]) K. MARTIN, Samml. des Geol. Reichsmuseums, Leiden, 1, p. 8—64, 1881.

section, described by R. JONES and CHAPMAN [1]). Afterwards SCHLUMBERGER [2]) has applied this name to a well-known form of Java, the thin section of which corresponded very well to the form of Christmas Island *d* 12—19 mm. *h* 5 mm. Skeleton columns very fine with little warts at the surface. This form is likewise known in Borneo[3]) and Sumatra [3]).

A rather large form of *O. formosa* first described by SCHLUMBERGER [4]) as *O. formosa* is likewise well known. From the sections (he found the Orbitoide in hard lime-rock), he concluded that he had to do with a radius-shaped Lepidocyclina, but DOUVILLÉ [3]) showed that the Orbitoide had a very pronounced saddle-shape, and consequently gave a radius-shaped horizontal section — megalospheric, median chambers on horizontal section half-circle-shaped, lateral chambers separated by very thin horizontal parietes *d* max. 18, *h* 2 mm. At the surface no warts are found. Borneo [3]), [4]), and Celebes [3]).

The microspheric form of *O. Tournoueri* LEM. and DOUV. is likewise large and according to DOUVILLÉ [3]) likewise smooth.

5. Orbitoides of average size. Not many forms of average size remain. BRADY [5]) described from the Padangsche Bovenlanden an Orbitoid as O. papyracea, afterwards VERBEEK and FENNEMA[6]) proved the incorrectness of this determination and called the form which they knew likewise from Nias *O.* 1 *B.* NEWTON and HOLLAND [7]) found this Lepidocyclina back in Sarawak and christened it O. VERBEEKI. They found there both the microspheric form, and the macrospheric one, the former is the larger *d* 5—12 mm. *h* 1$^1/_2$—2 mm. By the smooth surface and the gradual thickening towards the centrum this form is sufficiently characterized; it can only be mistaken for O. formosa. Incidentally O. VERBEEKI is likewise mentioned from Christmas Island [8]).

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[1]) T. RUPERT JONES and F. CHAPMAM, l.c. p. 242—243.

[2]) C. SCHLUMBERGER, Samml. des Geol. Reichsmuseums in Leiden, 6, p. 128—134, 1901.

[3]) H. DOUVILLÉ, l.c.

[4]) C. SCHLUMBERGER, Samml. des Geol. Reichsmuseums in Leiden, 6, p. 250—253, 1902.

[5]) H. BRADY, l.c.

[6]) R. VERBEEK et R. FENNEMA, l.c.

[7]) BULLEN NEWTON and HOLLAND, l.c

[8]) JONES and CHAPMAN, l.c.

At last, though very incompletely, a new species from Christmas Island is described by JONES and CHAPMAN as *O. Andrewsiana*. There is only a median tubercle *d* 9.75 mm.

At last from a great number of places the subgenus Lepidocyclina is mentioned, the forms however could not definitely be determined, these places are Java 1), N. W. Guinea 2), Koor 2), Batjan 3), Obi 3) and the Philippines 4).

Of all authors only H. DOUVILLÉ has tried to make use of the Indian Lepidocyclinas as leading fossils, in doing which he supports himself on experience gathered elsewhere. He gives the following table:

Burdigalien	L. Tournoueri, L. sumatrensis.
Aquitanien sup.	L. insulae-natalis.
Aquitanien inf.	L. formosa.
Stampien	L. formosa, with Nummulites subbrongniarti.

In the following description of our material we shall combine the sorts that belong stratigraphically together, beginning with the oldest, so that we shall be able to see, whether our results agree with those obtained by DOUVILLÉ.

O. (Lepidocyclina) aff. formosa SCHLUMBERGER.

In a lime-marl, about 2 km. West of the Kampong Pamaluan occurred, besides small Orbitoides, other Foraminifera and corals, many splendidly conserved large Orbitoides, which could be washed out in toto from the marl, so that it was easy to prepare orientated sections.

The scale is flat, circular (*d.* 23 mm.) and provided with a median tubercle (*d* 4 *h* 3.5 mm.). Most scales are flat, some however show a saddle-shaped bend. At the surface one easily discovers the lateral ventricles bordered by polygons, whilst at the edges one can here and there see the median chambers dimly shining through. Scarcely any vestiges of skeleton-columns are to be seen at the surface.

Horizontal section. Two horizontal sections have cut the median chambers in various sectors. These are more or less spatulate. The embryonal chamber is not touched; it must however be very small,

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1) K. MARTIN, Samml. d. Geol. Reichsmuseums in Leiden, 6, p. 135—245, 1902.

2) K. MARTIN, Samml. d. Geol. Reichsmuseums in Leiden, 1, p. 65—83.

3) K. MARTIN, Samml. d. Geol. Reichsmuseums in Leiden, 7, p. 225—230, 1904.

4) K. MARTIN, Centralbl. f. Mineralogie etc. 1901, p. 326—327.

as the other chambers reach to the immediate vicinity of the centrum. Most of the central chambers that are next to the embryonal one are flattened in a radial direction, the radial diameter is 40—60, the tangential one 60—80 μ. Only farther towards the periphery the median chambers become pretty regularly six-angular, whilst the most peripheric ones are spatulate In general the size of the chambers increases towards the periphery, but occasionally rings of smaller chambers occur between larger ones. Whilst by far the greater part of the median chambers are ranged in circles, their arrangement in the centrum is a little more irregular, and at the periphery sometimes not continued curves are linked between the continued concentric circles. The number of concentric circles of median chambers amounts to more than 100. The radial diameter of the peripheric chambers is 150—250 μ, their tangential diameter 140—150 μ. Especially at the periphery the parietes of the median chambers show a typical structure (fig. 1). The parietes namely consist of a dark untransparent central lamella to which granular, grey calcite sticks. In this section the central lamella is not continued round the chambers, but consists of a tangential, peripherial curve, two tangential, central parts of a curve (each the half of a tangential peripherial curve of chambers placed more towards the centrum) and of two radial lamellae, ending towards the centre in a tangential curve. Perhaps there is above this little curve a porus of a tangential shape uniting the chambers of the same curve. In many ventricles the central lamella is on all sides covered by symmetrically thick secondary parietes, in others these secondary parietes are thinnest on the tangential parietes.

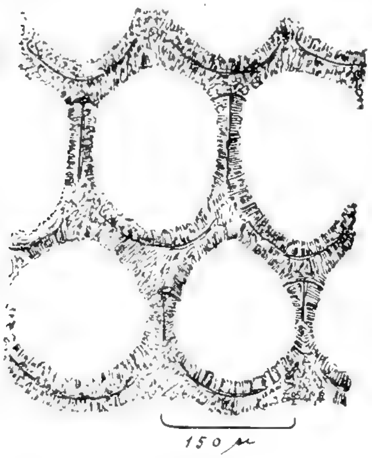


Fig. 1.

Vertical section. From this section appears likewise that the embryonal chamber must be very small, though it is not visible itself. The height of the median chambers namely decreases from the periphery to very close to the centre from 120 to 60 μ. The peripherical parietes of the median chambers are always convex to the outside, the structure of the parietes is only very unsatisfactorily visible. The lateral chambers have very thick parietes, and are strongly flattened in a vertical direction; their height is 30—50 μ the thickness of the parietes 30—40 μ. Because the parietes are regularly laterally interlocked, more or less vertical thickenings of the parietes are formed slightly diverging from the centre, which are imperfectly developed skeleton-columns. On either side of the median plane are in the centrum about 20, at the periphery only 5 strata of median ventricles.

In a dense, grey limestone, which is found half way to the top of the range of mountains containing the spring of the Sepaku, I found many Orbitoides, showing in the main great resemblance to those just described. The shape of the median chambers, the structure of their parietes, their dimensions and likewise the shape and situation of the lateral chambers are completely alike. The largest diameter is 23 mm. Only the shape of the embryonal chamber, which like the second chamber is very large, shows a great difference. Both these chambers communicate with each other by a very wide opening.

The two described Orbitoides consequently form a distinct pair: the fossils of the Pamaluan are the microspheric, those of the Sepaku the megalospheric forms.

There are only very slight differences between the described form and O. formosa. The inferior and rare, saddle-shaped bend of our Orbitoides is of little importance, it is well-known that in this respect many sorts are very variable. SCHLUMBERGER (l. c.) however reports about O. formosa, when describing the lateral chambers, that these are: "très surbaissées et séparées par de très minces parois", whilst in our form the horizontal parietes between the lateral ventricles are very thick. S. communicates too little about the shape of the median chambers to enable us to discover eventual differences with our form.

In the lime-rock of the Sepaku-spring-mountains occurs another little Lepidocyclina that cannot be more exactly determined, besides the Orbitoid described; further Globigerina, and most likely Textularia. The limestone is grey and rather transparent on the section; it contains here and there microscopic grains of pyrite, which often fill the ventricles of Orbitoides.

In the marl of the Sungei Pamaluan a few more smaller Lepidocyclina were found (5 specimens) whose diameter was only 5 mm., in one case even less. The median chambers are rhombic on the horizontal section, most likely the embryonal chamber is small. The skeleton-columns at the surface have the appearance of small warts, the situation and number of which vary strongly even in this insignificant material. In two specimens there was only one central wart, two others showed many warts scattered all over the disk, whilst in the last specimen only a few warts lie round the centre. In general these characteristics agree very well with what is known of *O. neo-*

dispansa JONES and CHAPMAN (O. dispansa BRADY and O. 1 A VERBEEK and FENNEMA); the material is however too insignificant to admit of a reliable determination. It is however of importance that we find in a level characterized by a frequent occurrence of a primitive Lepidocyclina, likewise a few representatives of types younger according to DOUVILLÉ (l. c. p. 449). Perhaps it is likewise remarkable that these younger forms show here evidently great variety in one important characteristic, (the wart-shaped appearance of the skeleton-columns at the surface).

From a lime-marl at the Sungei Blakan by washing a great number of Foraminifera were obtained, the greater part of which belonged to Orbitoides. From this rough material the different sorts could now be selected, and it appeared that in this way strongly separated series of forms could be obtained, it was but seldom doubtful among which group a definite specimen ought to be ranged.

With great application and perseverance my wife performed the fatiguing work, taking up so much time of washing and selecting the sorts.

The sorts collected here are the following:

O. (Lepidocyclina) acuta n. sp.

Of this sort about 50 specimens were found the horizontal diameter of which varied from 3—7 mm. One sees at the surface the irregularly bordered lateral chambers, whilst at the edge sometimes the median chambers are likewise visible, as here the lateral ventricles may be missing. The centre of the disk is taken up by a single skeleton-column which is sometimes diffuse and variable in size, and can likewise consist of an agglomeration of small columns. There are no other skeleton-columns placed nearer towards the periphery. The central part of the disk is strongly drawn out in a vertical direction, so that the Foraminifere is pointed at both extremities, which gives to this Orbitoid a very peculiar shape (acuta). The fact that these skeleton-columns are restricted to the lengthened vertical axis is obviously very appropriate. This lengthening in a vertical direction is however subject to many variations; it can be so important, that the vertical diameter becomes longer than the horizontal one (I measured in one case *d* 3 *h* $3^1/_2$ mm.). The peripheral edge is with this form always flat never bent saddle-shaped.

Horizontal section. Neither could I observe the embryonal chamber here; it must however be very small, as the median chambers reach to the immediate vicinity of the centre. The more central median chambers are flattened in a radial direction (rad. diam. 17, tang. diam. 30 μ). In these chambers already the parietes are thick (10 μ); only an indistinct central lamella can be observed in the parietes.

Towards the periphery the chambers become first hexagonal afterwards spatulate; in these peripheral chambers the cavity of the ventricle however always remains oval. It is very typical that with this form, the chambers are placed so irregularly, so that very often not continued curves are linked between the concentric circles. The dimensions of the peripheral chambers vary considerably; radial 65—90 μ tang. diam. 55 μ. The number of concentric rings of chambers is more than 50 and less than 100. At some places of the preparations the more delicate structure of the parietes could be studied. Here likewise a central lamella can be distinguished which is however often indistinct. The secondary parietes are here separated much sharper from the later chamber-filling than with O. formosa, which however may partly be a consequence of the conservation. Here namely every chamber is filled with single crystal of calcite, whilst by O. formosa the ventricles were usually filled with an aggregate of exceedingly fine crystals of calcite. At some places the wide pori can be seen that lead from one median ventricle obliquely outward to two median chambers of the ring lying more peripherally. Numerous pori run from the median chambers vertically or somewhat obliquely upward and downward to the adjacent lateral chambers. In the main the shape of the central chambers is the same as with O. formosa; the radial parts however are continued here as far as the periphery (fig. 2).

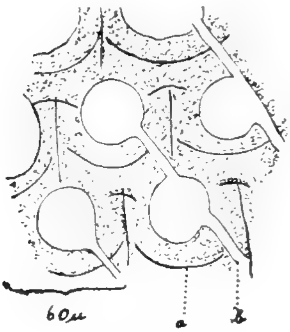


Fig. 2.

Vertical section. In the vertical section one sees very distinctly the increase of the vertical diameter; the strong, central skeleton-column is especially on one side clearly represented. The system of the median chambers consists of only one stratum, the chambers are low (45 μ) and their horizontal parietes are very thick (25 μ). The pori between the median and the lateral chambers are represented here lengthwise; it appears likewise that the lateral chambers communicate with each other by means of many wide, vertical pori, which are partly infiltered with a brown mineral containing Fe. The number of strata of lateral chambers on both sides of the median plane amounts to about 20.

O. (Lepidocyclina) flexuosa n sp.

A second form of Sungei Blakin is somewhat less numerous than the former, I could dispose of about 20 specimens agreeing very well with each other. The Foraminifera consist of a lens-shaped body surrounded peripherally by an edge which is strongly plaited in a vertical direction (flexuosa). The horizontal diameter is 4—7 m.m. the vertical one about 3 m.m. At the surface one sees distinctly, especially in the centre, the wart-shaped extremities of many not thick skeleton-columns between the lateral chambers enclosed in irregular polygons.

Horizontal section. On account of the strong bend of the median plane in a horizontal section of course only irregular areas of median chambers can be hit. Again the embryonal chamberlet must be very small; it is however not hit in a single section. The first peripheral chambers lie irregularly round the centre; those lying farther outside seem to be placed in regular concentric rings. Near the centre the median chambers are again flattened in a radial direction; *d* 40μ rad. and 55μ tang. More towards the periphery the median chambers become first hexagonal, afterwards rhombus-shaped or spatulate, it seems that the rhombus-shaped chambers have the majority. The dimensions of these peripheral chambers are: *d* 20—120μ rad., 60—100μ tang. The number of concentric chamber-rings amounts to 50—100.

Likewise in this form a primary lamella can be distinguished at the parietes of the median chambers, the secondary thickenings of the parietes change here gradually into the later chamber-filling. The shape of the median lamellas is typical, each ventricle is bounded by a peripheral arched piece, that passes into two radial parts whilst at the central side two arched pieces are found (fig. 3). Pori between the median chambers could not be discovered with certainty.

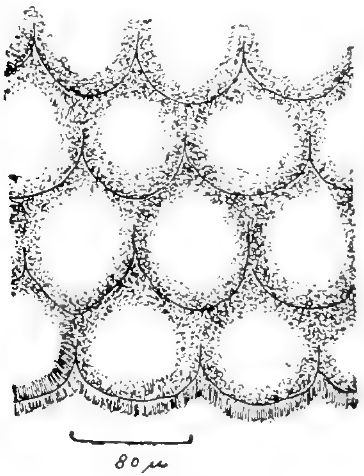


Fig. 3.

The lateral chambers are in this section likewise enclosed in irregular polygons, their parietes are very thick; they correspond by means of rare, very wide, horizontal pori, whilst at favourable places one sees exactly into the openings of numerous vertical pori.

Vertical section. Whilst in the centre there is but one stratum of median chambers, they gradually increase towards the periphery, so that there 2 or 3 strata of median chambers are found. From the centre several skeleton-columns extend towards the periphery, others are linked in at half-height. The height of the median chambers in the centre amounts to 25μ. The lateral chambers are here likewise strongly flattened, and communicate with each other by numerous vertical pori. The number of strata of lateral chambers at the centre is about 20 or more, at the periphery it is sometimes 0.

The Lepidocyclina described has the greatest resemblance to O. multipartita Mart., but differs again from it by a smaller size, greater thickness, inferior extension of the median plane towards the periphery and by the small embryo-chambers. Neither can O. flexuosa be regarded as the microspheric form of O. multipartita, as the microspheric forms are always larger than the megalospheric ones. From O. insulae-natalis the described sort distinguishes itself by its smallness and general shape, from O. neodispansa by its thickness and the much less great warts.

O. (Lepidocyclina) polygona n. sp.

A form that is no longer round but more or less regularly polygonal (polygona) contrasts very strongly with the two former. It is a little thin Lepidocyclina (d $1^1/_2$—3 mm., h 0.9 mm.) of a trigonal to hexagonal shape. At the surface one sees distinctly the irregularly confined chambers, whilst at the angles comparatively very strong columns in the shape of warts, are found at the surface. Among my material there was only 1 specimen with 3 warts, 40 with 5 warts and 13 with 6. As a general rule may be admitted, that the number of warts and consequently likewise the polygonamy increases with the size, yet there are many exceptions to this rule.

Median horizontal section. In impure median sections one sees the irregularly confined, lateral chambers and the skeleton-columns, consisting of an aggregate of crystals of calcite. Here and there pori running vertically or obliquely upward can be seen between the lateral chambers.

The embryonal chamberlet is very large, the second chamber is still larger and partly encloses the former; the exterior parietes of these two chambers are thick, the separating parietes between these two chambers are very thin. The maximal diameter of the second chamber amounts to 300—400 μ. Though in general the median chambers in this genus are still spatulate, their shapes vary however considerably, whilst they are moreover placed very irregularly; it is difficult to find back here the concentrical rings. The parietes of the median chambers are always thick; there was no vestige of a primary central lamella. Very numerous pori run vertically or obliquely, even horizontally, from the median chambers to the lateral ones.

Vertical section. There is but one stratum of median chambers, the height of the ventricles is 35 μ, the thickness of the horizontal parietes 10 μ. It is very distinctly to be seen how the skeleton-columns begin only at some distance from the median plane, and become gradually thicker towards the periphery. On either side of the median chambers are only 11 strata of lateral chambers.

O. (Lepidocyclina) sumatrensis Brady.

This form is by far the most numerous at the Sungei Blakin. It can very easily be distinguished from all other forms of the same place; with O. sumatrensis, which has been minutely described especially by Newton and Holland (l.c.) it shows only slight differences, which are not sufficient to make a new species of it.

The disk has never or scarcely ever warts at the surface, it is very thick (*d* 2—4, *h* 2—2, 7 mm.) and sometimes even cylindric. In the middle, one can follow a thin wedge often ending in flaps.

Horizontal section. This form is megalospheric; the embryonal chamber is partly surrounded by the second chamber, just as with O polygona and the little Orbitoides of Timor described by Martin (l.c.). The outer-parietes of these two chambers is 33 μ thick; the separating parietes between the two chambers only 10 μ. The maximal diameter of the embryonal chamber, is 190 μ, that of the second chamber 310 μ. The median chambers are more rhombus-shaped than spatulate, situated in rather regular concentric rings, often lengthened in a tangential direction. Their diameter is tang. 90, rad. 60—70 μ. The median lamella is indistinct. The number of concentric rings is 30—50.

The shape of the lateral chambers is not so irregular as with the greater part of Orbitoides; they are also placed in rather regularly concentric rings, which is likewise mentioned by Newton and Holland (l.c.) about O. sumatrensis.

Vertical section. There is only one stratum of median chambers and on either side of these 15 strata of lateral chambers. Though at the surface no warts can be observed, it appears that there exists doubtlessly in the interior a firm interjacent skeleton. The height of the lateral chambers is 70 μ, the thickness of the horizontal parietes is 30 μ.

Subgenus novum Lepidosemicyclina.

Besides the Orbitoides described I found in the marl of the Sungei Blakin still numerous Forminifera, which offer in several respects great affinity with Lepidocyclina. With those too a system of median chambers exists, which in general have on the horizontal section a spatulate shape, and develop themselves round a few large embryonal chambers; with those too on either side of these median chambers there are lateral ventricles, of an irregular shape, and between these a supporting skeleton is found, ending at the surface in numerous warts. In one respect however these forms show great differences with Lepidocyclina: the median chambers namely do not lie in concentric rings, but only in half- or quarter-circles, in which the embryonal chambers are lying at the periphery, in the central point of the circle-sector. Consequently a new subgenus was introduced for these forms: Lepidosemicyclina.

Lepidosemicyclina thecideaeformis n. sp.

At the Sungei Blakin occurs only one species of this subgenus having usually the shape of a circle-sector of somewhat less than 180°, and being a little thickened in the central point of the circle, so that the little shells make us think of Brachiopod Thecidea. One side of the shell is often more convex than the other, the latter can even be concave, so that the horizontal median plane is no longer a pure symmetrical plane. At the surface there is no vestige of lateral or median chambers; the whole disk is covered with little densely accumulated warts. There is some variety in the general shape, because now the tangential, now the radial diameter is the larger, (2—4 mM.) Sometimes the shell is slightly bent, in most cases however quite flat.

Horizontal section. In a good section one sees distinctly the large embryonal chamber, which lies a little beside the central point of the circle. It is large and round, and its parietes are thick (d. 160 thickness of the parietes 20 μ). With this embryonal chamber is connected a still larger chamber, which lies at the extremity of the shell, i. e. in the central point of the circles and partly surrounds the embryonal chamber. Its peripheric parietis is still thicker than that of the embryonal chamber (30 μ); the borderparietis is only 15 μ thick. Two more large chambers, lying more to the centre, are connected with this second parietis; these three ventricles surround the embryonal chamber in an indistinct spiral. The following chambers are already rhombus-shaped. A primary lamella can never be distinguished at the parietes. Radial diameter of the peripheric chambers 100 μ tangential 90 μ. At thicker spots in the preparations one sees very distinctly the wide vertical pori going to the lateral chambers.

Vertical section. There is only one stratum of median chambers. In vertical section this stratum is rather slightly strung at the extremities of the chambers. On either side of it are 5—6 strata of lateral chambers, which are very flat and placed on each other somewhat in the way of scales. The thickness of the fossil is 0.8 mm.

Besides the Foraminifera mentioned I found in the marl of the Sungei Blakin: Operculina spec., Amphistegina spec.? Cycloclypeus spec., and other Foraminifera, which I could not determine.

The third place where numerous Orbitoides could be gathered, lies on the upper-course of the Sungei Mentawir in strata that are certainly younger than those on the Sungei Blakin and that most likely, towards the top gradually pass into the pliocene strata, very rich in coal, which occur everywhere in the lower part of the Balik Papan Bay.

O (Lepidocyclina) sumatrensis Brady, var. minor nov. var.

Most numerous is here again a very small Orbitoid agreeing in nearly every respect with O. sumatrensis of the Sungei Blakin. The principal difference consists in the fact that the sort on the Sg. Mentawir is considerably smaller (d $1^1/_2$—2, h 1, 2– $8^1/_2$ m.m.) This cannot be accidental, because we should have gathered from this place only the smallest varieties: the material gathered in both places being much too large. For the further description we can refer almost entirely to O. sumatrensis. Only no or hardly any skeleton-columns occur with the form of the Sungei Mentawir, which would indeed be astonishing with so small a form which by its globosity possesses already a natural maximal solidity.

O. (Lepidocyclina) neodispansa Jones and Chapham, var. minor, nov. var.

I can dispose of about 20 specimens of this form tallying very well with one another. In general these have again great resemblance to O. neodispansa. The disk is gradually thickened towards the middle and a number of comparatively large warts (max. 20

indicate the superficial end of the skeleton-columns. They are however smaller than O. neodispansa: $d\ 1^1/_2$—3, $h = 1$—$1^1/_2$ mm.

Horizontal section. The embryonal chamber is large and has thick parietes (d max. 270, thickness of the parietes 20 μ). The chambers round it are half-circular, and further towards the periphery pretty well rounded hexagonal, but always irregular. It is very typical that the median chambers at the periphery are not placed in concentric circles, but in the circumference of concentric hexagons, the sides of which are somewhat concave to the outside. Horizontal pori between the median chambers are not visible, but very many vertical pori can be observed. The lateral chambers are irregularly limited and have a wide lumen. They are united together by many almost horizontal pori. The diameter of the median chambers is 45—50 μ; the thickness of the parietes 15 μ.

Too little is known of the interior structure of O. neodispansa to enable us to decide whether the described form agrees in every respect with this sort; the resemblance in outward characteristics however is so great that I have not hesitated to describe these Lepidocyclines of the Sungei Mentawir as a variety of O. neodispansa.

O. (Lepidocyclina) glabra n. sp.

Ultimately about 15 specimens of a somewhat larger Lepidocyclina were collected at this place, characterized by the indistinctness or even the absence of superficial warts. By its form it has the greatest resemblance to O. neodispansa (d 2-5, h 1-2 mm.), but the absence of warts forbids us to class it with this form.

Horizontal section. Likewise by its microscopic structure this sort is obviously separated from those hitherto described. Most likely the embryonal chamber is large, the first peripheric median chambers are irregularly roundish; towards the outside however the chambers become soon spatulate and show a peculiar typical central lamella which has the same shape as that of O. flexuosa, but is much thicker (fig. 4). Perhaps there are in this primary lamella very fine channels. Rad. diam. of the median chambers 45, tang. 35 μ.

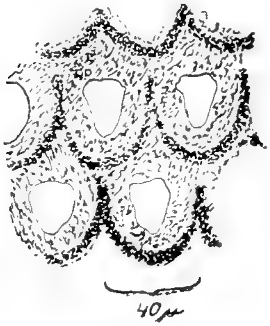


Fig. 4.

Lepidosemicyclina polymorpha n. sp.

In the younger strata of the Sungei Mentawir we meet with a form of Lepidosemicyclina, corresponding in structure entirely to the older form of the Sungei Blakin, so that we can refer to the latter. Externally the young form differs greatly from the primitive form, especially by its great variability. Some forms are found that can hardly been distinguished from L. thecideaeformis, other specimens are strongly plaited, scalloped at the peripherical edge, are considerably protracted in a radial direction and have even a quite irregular shape.

There are some features that point very vaguely to the fact that thecideaeformis was able to creep, whilst L. polymorpha had become fastened. Whilst namely the other Orbitoids are constructed radially, which with great probability points to a floating way of living (plankton) L. thecideaeformis has not only become bilaterally symmetric in a vertical direction, but has also obtained an upper- and a lower-edge (difference in convexity) and has consequently adopted the symmetry we are accustomed to find in creeping animals. Hereto comes however that the younger form shows so great a variability and such irregular forms as we are only accustomed to see of animals that are fastened (Ostrea).

Besides the Orbitoids described we find in the marl of the Mentawir still Amphistegina.

In a few words we shall still discuss rocks of other finding-places containing only generically determinable fossils.

As old as the clay-marl on the Sungei Pamaluan is a limestone, found on rather a large scale in the delta of the mentioned river. Herein the vertical section of a little Orbitoid, a Globigerina and perhaps also Amphistegina was found. The limestone is very compact, becomes scarcely transparent under the microscope and contains occasionally grains of pyrite.

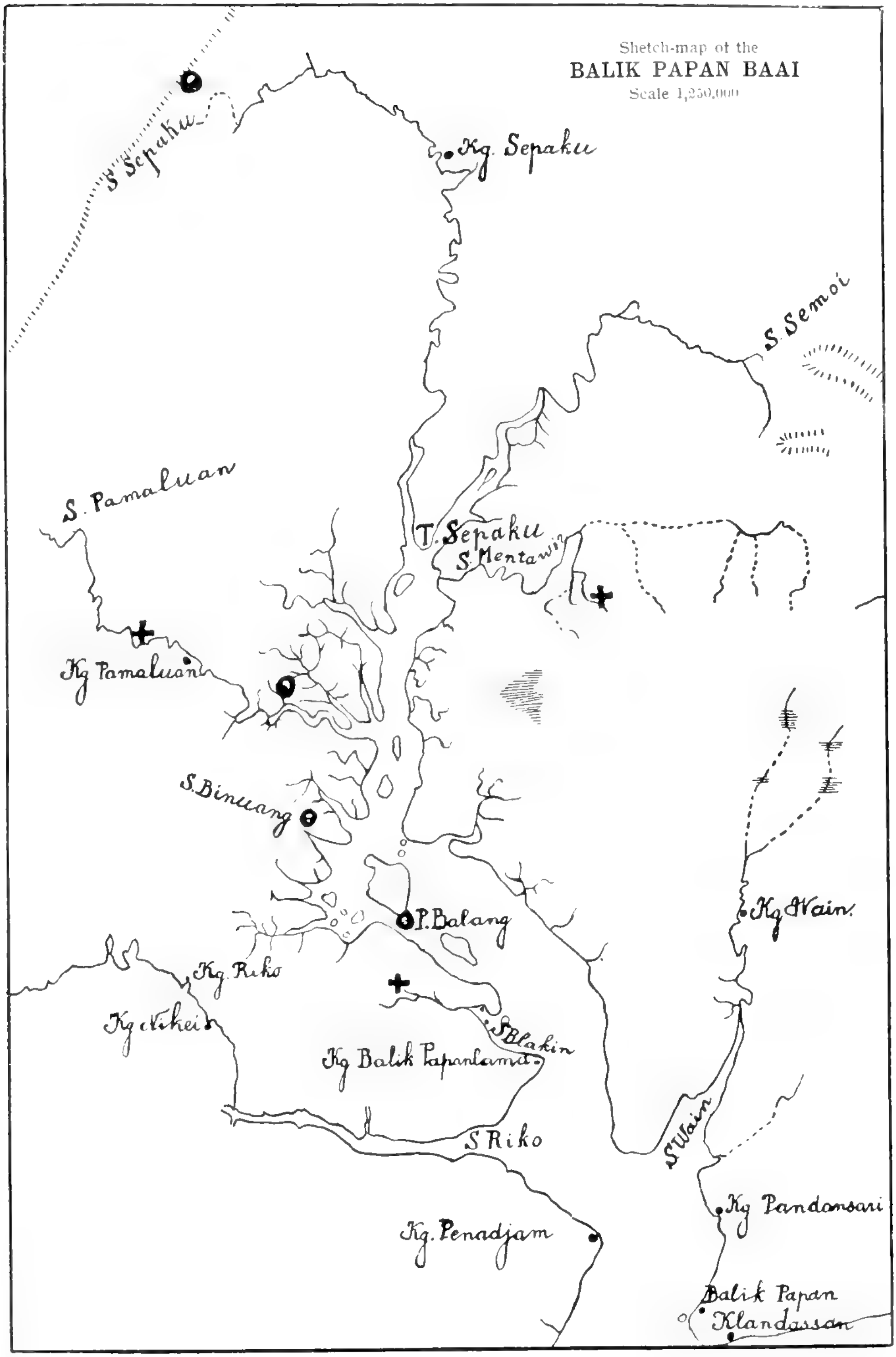
Younger than the Pamaluan-marl, but perhaps older than the Blakin-marl is a marly sandstone, found on the Sungei Binuwang.

Under the microscope the marl appears to consist of polygonal grains of quartz united together by a cement rich in Fe- and Ca. It contains Amphistegina, a single Alveolina 5 mm. long, a few Orbitoides and a large spiral-shapedly constructed Formanifere (not Spiroclypus) entirely unknown to me.

A marl that is found on the S. E. coast of Pulu Balang and of which a specimen contains a large enclosure of resin is entirely filled with Foraminifera, among which: Miliola, a very small Alveolina, Globigerina, Amphistegina, a small Orbitoid and others can be recognized. The marl contains many polygonal grains of quartz, whilst the fossils often enclose grains of pyrite.

Consequently the Orbitoides described above may be classed into

L. **RUTTEN**. "On orbitoides in the neighbourhood of the Balik-Papan Bass (East-coast of Borneo)."



three different divisions of the Tertiary on the Balik Papan Bay:

Mentawir strata	L. sumatrensis var. minor, L. neodispansa var. minor, L. glabra, Lepidosemicyclina polymorpha.
Pulu Balang-strata (Sungei Blakin)	L. acuta, L. flexuosa, L. sumatrensis, Lepidosemicyclina thecideaeformis.
Pamaluan-strata	L. aff. formosa, L.? neodispansa.

The stratigraphical succession thus obtained does not entirely agree with the one given by H. Douvillé. It is true that with us in the oldest strata occur simple forms of the type L. formosa, but beside these immediately forms of the type O. neodispansa are found, which according to Douvillé must be much younger. On the Sungei Blakin occur then beside each other forms with strongly and feebly pronounced skeleton-columns (O. flexuosa) forms of the type of L. sumatrensis, and forms with one single, large, central wart, which according to Douvillé should occur in separate horizons. The same holds for the youngest strata, the Mentawir-strata.

It is however remarkable, that in the oldest level the simplest forms occur, that in the middle level the number of species is greatest, and that in the youngest level, which cannot be much older than the dying-out-period of the genus, two minor forms occur, whilst of a third species very peculiar variations are found.

Zoology. — "*Observations on the Genus Spirastrella*". By Prof. G. C. J. Vosmaer.

(Communicated in the meeting of March 25, 1911).

Oscar Schmidt established (1868) the genus *Spirastrella* for a "new species" of Siliceous Sponge, the chief character of which was said to be that it possessed an "eigenthümliche Art von strahligen Kieselkörperchen, deren Strahlen spiralig gestellt sind." We now know that that sort of spicules is by no means of rare occurrence, and that it does not represent a special form of polyaxons, but of monaxons; such spicules are now called spinispirae. In addition to these spicula the skeleton of *Spirastrella* is composed of tylostyles or also of styles. Since Schmidt described his *Spirastrella cunctatrix,* various authors have mentioned numerous "species"; all in all about 44. But of these, ten are to be cancelled at once, either because they do not belong to our genus at all, or because they are quite inadequately described, so that they are not recognisable.

In the rich collection of the Siboga Expedition I found about a hundred specimens of Siliceous Sponges, which I believe belong to the genus *Spirastrella*. I examined them as carefully as circumstances allowed; moreover I studied about forty specimens from other localities, chiefly types of previous authors and for the greater part deposited in the British Museum. The result of this research is that I am convinced that we have to do with an uncommonly variable species; 32 of the 34 "species", described by previous authors, and all the specimens of the Siboga collection belong to one single species, which, according to the rules of priority, has to be called *Spirastrella purpurea* (Lmk.) Rdl.

If we look at the specimens macroscopically, we at once see differences so great, that any one would expect to have to distinguish a number of "species". Sometimes they appear as thin encrustations on old pieces of coral, coralline algae etc., sometimes as thicker cakes with warty elevations. Another time they are club-shaped, or cylindrical with finger-shaped terminations, or cones, or pyramids. Others again have an irregularly spherical shape and form massive lumps. The colour is pale or bright yellowish, brown, grey; sometimes bright carmine red. Among the encrusting forms some are no more than 1 or 2 mm. thick; on the other hand we find massive specimens of 12 by 18 cm.; nay BOWERBANK mentions one, which reached a height of almost 2.5 meters. The surface is even, or provided with warty or digitiform elevations; smooth or hispid.

However, if we more carefully examine the specimens and then try to classify them into groups, we soon come to difficulties and we find e.g. specimens which might be placed in one group as well as in another. Thus we find that some crusts are on the whole very thin, but nevertheless show here and there thicker regions; in fact we see the thin crusts gradually pass into thick cakes, or into specimens with warts, tubercles or finger-like processes. In some cases these processes have all about the same size; in other cases there is one main process with a number of smaller ones around it, gradually leading in this way to pyramidal cones with or without a few secondary processes at the base. Again in other cases the cylindrical processes are so long and numerous that they form the most characteristic feature of the sponge. Moreover, we may observe another phenomenon, viz. that neighbouring processes coalesce; in fact we see e.g. clubshaped specimens pass into spherical, massive forms.

From this state of things results the impossibility of making "species" on account of the external appearance; the extremes are united by all possible connecting links.

How is it now with the internal structure? The answer to this question is that we find here similarly great differences, but likewise all gradually passing into each other. This is true as well with regard to the canal system, as to the structure of the parenchyma and the skeleton, even with respect to the elements of the latter, viz. the spicules. I do not wish to discuss now these points in extenso; I will give a couple of examples, as I did regarding the external habitus.

It is characteristic for *Spirastrella* that the skeleton consists of longitudinal bundles of spicules, chiefly tylostyles, branching towards the periphery; between these bundles, but more especially forming a superficial crust, we find the well known spinispirae. It is a remarkable fact, that this represents the *complete* skeleton; under certain circumstances, however, the spinispirae may become very scanty and may even disappear altogether. In the latter case the character from which the genus has received its name, is absent [1]). In the papers of almost every spongiologist we find that species are distinguished e. g. on account of the size of the spicules. In our case the size of the tylostyli shows considerable differences. The maximal length I found in my specimens to oscillate between 280 and 800 μ., whereas the maximal diameter varies between 5 and 30 μ. Nevertheless, the extremes are united by all possible intermediate stages; no limits can be drawn for specific distinction. There are, however, certain sizes which prevail. The maximal length is in about 33 °/0 cases 550 μ and more, but less than 600 μ; in about 75 °/0 cases 500 μ and more, but less than 650 μ. Cases of less than 350 μ or more than 700 μ are rare. And so I found in 20 °/0 cases the maximal diameter of the tylostyli 16 μ and more, but less than 22 μ. I seldom found it less than 6 μ or more than 24 μ.

Still more striking are the differences of the spirispirae. We have already seen that these characteristic spicules sometimes occur in great abundance, at another time are exceedingly scanty. Thus I found in some specimens that one microscopical preparation of spicules, isolated by means of hydrochloric or nitric acid, contained a couple of spinispirae, whereas another slide of the very same specimen contained not a single one. Dendy found in his *Suberites inconstans* var. *globosa* and var. *maeandrina* no spinispirae. I was able to examine Dendy's types in the British Museum and did find them. Such facts are by

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[1]) This phenomenon is by no means seldom in the animal kingdom. It may perhaps be compared with the absence of a chorda in certain Chordata. The more so as I have reason to believe that the said spicules are present in larval or young stages, but afterwards disappear.

no means standing alone; they are examples of very numerous cases. This implies, however, that, if in certain specimens, externally corresponding, in one we find spinispirae, in another not, we have not the slightest right to establish new species or genera on account of the presence or absence of spinispirae. It is beyond doubt that DENDY's sponge is not a *Suberites* but a *Spirastrella*.

Now we find spinispirae of every description [1]). In many specimens of *Spirastrella purpurea* we find in addition to minute (but full grown) spinispirae of say 8—10 μ length, large robust ones of about 12 μ in diameter by a length of 75 μ. In other specimens such giants are missed altogether. At the beginning of my investigations I believed I should be able to find specific characters on this account. But I was forced to give up this view; for those large spinispirae sometimes measured a good deal less than stated above, or they possessed the length but not the diameter. In this respect again we find gradual transitions. These facts and the fact, that robust spinispirae are sometimes abundant, sometimes scarce or absent, teach us that we cannot yet establish species on account of the presence or absence of large spinispirae in addition to the minute ones. We have as little success if we try to distinguish species by certain microscopical details. LENDENFELD described a "new species" because of the fact that the spines of the spinispirae did not terminate in a sharp point, but showed a curious very minute denticulation. I found, however, on carefully studying the spicules with oil-immersion, that the "Efflorescenz-artiges Aussehen" appears in numerous specimens of the most various external appearance.

Summa summarum: we have to face the dilemma either of considering all the examined specimens as one species, or to establishing almost as many species as we examine specimens. I for my part do not hesitate which way to go. At present, at all events we still know very little about the comparative anatomy of Sponges and hardly anything about their comparative embryology. And yet these lowest Metazoa deserve to be studied carefully. Although they throw but little light on phylogenetic questions, and perhaps will never do so because they are an aberrant branch of Metazoa, in other respects I am convinced the Parazoa are certainly of general importance. For instance on account of their tissues. But the field of Spongiology is unexplored except by a few specialists. Not quite without reason, for there are many traps.

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[1]) Since it is impossible, for the moment, to make out whether we have to do with one or with more sorts of spicules, I consider them for convenience' sake as one kind.

If we can accept but one species of *Spirastrella*, the question arises whether perhaps certain groups of specimens point to a closer relationship to each other? Is it possible to distinguish groups according to the depth or to certain properties of the bottom on which they are found? The first question can be answered in a positive sense, the others not yet. Indeed I believe that about seven such groups may be distinguished, although by no means sharply, as they are all intimately connected. But if we unite a certain number of specimens which seem to be nearly related to each other, into groups and try to bring them into connection with their conditions of life, we soon find that hardly any conclusion can be drawn. For there are specimens from the same locality which do not belong to the same group; consequently we cannot speak of so-called local varieties.

The general structure of *Spirastrella purpurea* is, in spite of great differences, still fundamentally the same for various specimens. I will give a sketch of one form, viz. of a specimen corresponding to DENDY's *Suberites inconstans* var. *digitata*. A longitudinal section through one of the long finger-shaped processes shows us a central, more or less cylindrical cavity, generally opening at the top of the process. Such wide central canals are often met with in Porifera. The terminal opening is usually called "osculum" and the canal is considered to be of an excurrent nature. Indeed it is observed in many living Sponges that a current of water flows out from the "osculum", the water entering through numerous little apertures on the sponge surface. Microscopical examination of such Sponges has shown that the latter apertures communicate with "flagellated chambers". These chambers on the other side communicate again with a system of cavities, which open into the central canal, mentioned above. Now we know that the shape of the flagellated chambers and the position of the choanocytes determine the direction of the water-current. Consequently we can conclude from the shape of the chamber, which of the communicating cavities is excurrent, and which is incurrent. The whole canalsystem can thus be reconstructed by studying series of sections. This has been done for several Sponges, but not as yet for the majority. Since it was found in certain cases, that the large central canal belonged to the excurrent system, the conclusion was drawn per analogiam for other cases, that the said canal is excurrent.

However, in *Spirastrella purpurea* certain features seemed an obstacle to considering the central canal as a "cloaca". True, in several specimens the canal opened with a comparatively wide mouth, but in others the aperture is rather small. Moreover the canal is in most cases narrower at the top than lower down, and in many cases it is clearly seen, that the wide central canal towards the top of the process branches into a number of much narrower ones. Finally I found that the wall of the canal is not smooth, but shows several transverse rugae. Such a canal, according to the theory of PEKELHARING and myself, would be very little adapted to act as a cloaca. In view of all this I thought it necessary to reconstruct the canal system by means of series of sections. The result has been, that I found the positively excurrent canals not to communicate with the central cavity, but exactly the contrary: the incurrent canals communicate with it. Consequently, the central canal is not a cloaca but an incurrent reservoir. Numerous minute apertures (stomata) lead into a system of canals, which open in the central cavity, which also may communicate directly with the surrounding medium by means of a comparatively wide opening at the top of a process. From this reservoir canals start and enter, ramifying, the parenchyma; they ultimately communicate with the flagellated chambers or mastichorions as I have called them. As the canal system is eurypulous, the mastichorions open with a wide apopyle in the excurrent lacunae or canals, which finally likewise open at the sponge surface with small apertures, procts.

There is still another interesting feature in the canal system of *Spirastrella purpurea*. It is generally accepted that the principium movens for the watercurrent is to be sought for exclusively in the flagella of the choanocytes. In our sponge a second factor appears: in the wall of the larger canals, more especially of the central canal, numerous undoubtful muscle cells occur; they are situated in concentrical and in radial bundles. In the rugae we find the former in maximal dilatation. If on the other hand the concentric muscle cells contract the rugae are stretched out to a kind of membraneous diaphragms with the result that the lumen of the canal becomes considerably narrower. In some specimens this is in fact the case. Suppose that the terminal aperture has first closed, water must forcibly be pressed into the canals which lead to the inner parts and in this way the current-producing power of the flagella helped. In this connection it is worth while to remark that the total quantity of mastichorions is comparatively small.

The parenchyma is almost entirely composed of a remarkable tissue to which I more than once have drawn attention and which can best be compared with lymphoïd connective tissue. It consists of flat cells with delicate membraneous processes, forming together a sort of syncytium. At least I could not distinguish cell limits. In this way a reticulum is formed, the meshes of which are very different in size. In addition to these cells, fibres occur beyond doubt; perhaps also a kind of elastic fibres. For the rest we find cells of various description: amoebocytes, thesocytes, fusiform cells etc. The canals are lined with flat cells, which have exactly the character of the first mentioned cells; they may be considered as endothelium.

The skeleton is mainly formed by bundles of tylostyles. In encrusting specimens these bundles stand vertically on the substratum; they ramify generally towards the periphery and at any rate terminate in brushes. The spicules of the latter are usually smaller than the tylostyles of the main bundles. In massive specimens or those with finger-shaped processes long longitudinal bundles run through the parenchyma, here and there ramifying, occasionally anastomosing. These main bundles give off smaller branches towards the periphery; these as well as the main bundles terminate in more or less projecting brushes. Hence the sponge surface is now rather hispid, then smooth. On the whole we can say that the number of superficial tylostyles is in reverse ratio to the number of spinispirae. If the latter are abundant they form a "dermal" crust. If in addition to minute spinispirae robust ones occur, this crust is composed of one or two distal layers of the former and 2—5 proximal layers of the latter.

In many specimens with well developed longitudinal bundles, strings of darkly stained cells are seen at once in every preparation. These cells are more or less fusiform, possess a large nucleus and a large "nucleolus". They are found in close connection with the bundles of tylostyles. Most probably these cells are fibroblasts; they are the cells which form the connective tissue fibres, which strengthen the bundles of tylostyles by binding together the spicules. This tissue I have called periapt [1]); herein occur, in addition to fibres, fusiform cells etc. These fibroblasts which thus give rise to the fibres, are not always situated in such conspicuous strings; but they may be found everywhere, where fibres are to be formed or are normally present.

The occurrence of spinispirae, the arrangement of the canal system, the whole anatomical structure of *Spirastrella*, all suggests a close relationship to the so-called Boring Sponges, belonging to the genus *Cliona*. The two genera are, however, distinguished from each other by the fact that *Cliona* perforates calcareous matter (shells, corals, coralline algae etc.), whereas *Spirastrella* does not bore. Several speci-

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[1]) Proceed. Kon. Akad. Wetensch. 1905, p. 23.

mens of the Siboga collection are encrusting and sections of decalcified specimens simulate a boring sponge; in reality *Spirastrella* does not itself perforate, but easily fills up holes and slits of a calcareous substratum, destroyed by other organisms. As such I found e.g. *Thoosa* and certain Fungi [1].

Physiology. — *"The action of strychnine on the Central Nervous System. The segmental, strictly localized strychnine-intoxication of the dorsal spinal mechanisms: a contribution to the dermatomery of the hind leg in dogs."* By Dr. J. G. Dusser de Barenne. (Communicated by Prof. C. Winkler).

(Communicated in the meeting of February 25, 1911).

In a former communication [2] I endeavoured to prove that the theory, as if strychnine-tetani may have their origin in an intoxication by this alkaloid of the dorsal, co-ordinatory spinal mechanisms, is to all probability an erroneous one.

The application of the poison exclusively on the dorsal surface of the medulla, *never* gives rise to tetani as its consequence, but always to another complex of symptoms, which was described by me as the *Syndrome of strychnine-intoxication of the dorsal spinal mechanisms*:

1. Subjective disturbances of sensibility, most probably presenting a paraesthetical character.

(Finding their expression in the frog by "Abwischbewegungen", in the dog by licking and biting the skin).

2. Hyper-reflectory actions.

3. Spontaneous muscle-shocks, viz. arising without any exterior cause being observable, but still for the greater part proceeding in a reflectory manner.

Already with the first experiments it became evident that, whilst this complex of symptoms in itself is constant and characteristic, the skin-field in which these disturbances of sensibility (both subjective and objective ones) occur, is variable as to place and extension,

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[1] Extensive descriptions accompanied by illustrations, will appear in the Results of the "Siboga-Expeditie", which is in the press.

[2] Dusser de Barenne, Die Strychnin-wirkung auf das Zentralnervensystem. II. Folia neurobiologica. Band V, Heft 1, 1911. Provisory communication in Zentralblatt f. Physiologie. Band XXIV. N⁰. 18, 1910.

according to the different parts of the spinal cord on which the strychnine is applied.

If this poison is put on the caudal spinal segments, the symptoms are shown in the posterior portion of the body.

If I poisoned the dorsal mechanisms of the right half of the intumescentia lumbalis, the syndrome manifested itself exclusively in the right hind-leg.

In another case again the poison was applied on the dorsal surface of some of the caudal segments of the thoracal part of the medulla, after which the symptoms, described above, were manifested in a zone encircling the body like a band and passing over the most caudal ribs.

From these facts it becomes evident that the syndrome may be localized. It is even possible, if one after another the dorsal surfaces of single spinal segments are poisoned, to obtain a series of skin-fields, within which the syndrome is manifested, differing among them as to form, situation, and extension.

In this manner in a series of experiments, from *Th.* XIII to *S.* I included, I have poisoned successively the dorsal mechanisms of every single spinal segment and by so doing I obtained a number of skin-fields in which the syndrome (— paraesthesia concluded by the biting and licking of the skin-field, hyper-reflexion, concluded by violent reactions if the skinfield was touched) was manifested; those skinfields were placed in regular succession on the hindleg of the dog, their shape, situation, and extension being characteristic for each single zone. I will call these skinfields *strychnine segmental zones.*

As an instance of the way in which I proceeded in this series of experiments, as regards the method of the strychnine application, as well as the examination of the sensibility and the defining of these strychnine segmental zones, the protocol may follow here of one of my experiments on the caudal thoracal spinal cord; the more so because from the adjoined figures (fig. I—IV), demonstrating the results obtained in two cases of defining the boundary of the strychnine segmental zone of *Th.* X, it becomes clearly obvious how much for one and the same segment the zones resemble one another as to shape, situation, and extension.

I have chosen this experiment also, because the strychnine zones for the trunk segments are very simple as to shape, contrary to those situated on the extremity, and therefore showing with greater evidence their mutual resemblance.

Protocol I.

June 6th, '10. Str. Dog XVIII. "Daekel".

The caudal portion of the thoracal spinal cord is uncovered and the dura-mater cleft over *Th.* IX, X and XI, the liquor cerebrospinalis that has flown out, is sucked up by a bit of wadding. Then strychnin is applied in the following manner:

A small piece of wadding, long ± 3 mm., wound around the branches of a thin pair of nippers, is immersed in a 1 $^0/_0$ solution of sulfate of strychnine dyed with methylene-blue, and then pressed out.

With this piece of wadding the dorsal surface of the segment of *Th.* X, at the entrance-point of the right posterior nerve-root, is repeatedly bathed with the utmost carefulness.

After each contact with the strychnine wadding the superfluous poison that has eventually been applied, is sucked up by another, clean and moist piece of wadding.

A few seconds after the repeated contact of the poison with the spinal cord at this spot, the dog that meanwhile has nearly awakened from the narcosis, begins to lick the skin of the right half of the trunk over a region, extending like a band of moderate breadth from the mid-dorsal to the mid-ventral line, passing over the most caudal ribs.

The dog itself, with its moist tongue, marks pretty clearly the boundary of this zone. The objective part of the syndrome is likewise extant and may be easily aroused from out the same skin-zone. The hyper-reflectory symptoms are: 1. wrinkling of the skin, 2. curving of the vertebral column, the concavity turned to the right, 3. with intervals scratching movements of the right hind-leg, resembling closely those of the well-known SHERRINGTON's "scratch-reflex".

In order to obtain an objective definition of the extension of the strychnine-segmental-zone, I touch very gently the skin of the animal in the neighbourhood of the region within which the syndrome is manifested, either with one of my finger-tips, or with the point of a curved, shut pair of nippers.

Continually repeating this gentle, mechanical irritation, I gradually approach that region, and as soon as I have passed its boundary, the hyper-reflectory symptoms described above are aroused or become much more intense, whilst in most cases¹) the animal shows at the

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¹) I say "in most cases", because the intensity of the subjective part of the syndrome presents great variations in different cases, partly dependent on "temperament and character" of the animal, whilst for another part they may perhaps be ascribed to its more or less complete awakening from the narcosis.

same time by howling and biting that the subjective symptoms are likewise aroused or their intensity increased.

By means of a skin-pencil the boundary obtained in this manner is marked on the skin and so the zone defined. After this the animal is killed, and either the posterior part of the body is photographed, or the zone is exactly designed on a model in plaster of the extremity.

Firstly however on the skin resp. the plastermodel, the different fixed points and lines are indicated, viz. the last rib, the crista ilei, the trochanter major, tuber ischii, epicondylus femoris lateralis and medialis, patella, tuberositas tibiae and malleolus medialis and lateralis.

After this the autopsy is made, and in so doing it is accurately verified on which segment the poison was applied whilst an eventual anomaly of the vertebral column is also mentioned in the protocol.

Fig. I. *Th.* X.

Fig. II. *Th.* X.

Fig. III. *Th.* X.

Fig. IV. *Th.* X.

My material, as far as regards these researches, consists in 29 experiments, distributed over the different segments in the following way:

On the segment of

Th. X	strychnine	was	applied	3 ×	(Str. dog XVIII, XIX, XX)
Th. XIII	,,	,,	,,	1 ×	(Str. dog XLIV)
L. I	,,	,,	,,	1 ×	(Str. dog XLV)
L. II	,,	,,	,,	3 ×	(Str. dog XIII, XXV *L.*, XLVI)
L. III	,,	,,	,,	3 ×	(Str. dog XXI, XXIX, XLVII)
L. IV	,,	,,	,,	4 ×	(Str. dog XIV, XXV *R.*, XLVIII, XLIX)
L. V	,,	,,	,,	3 ×	(Str. dog XV, XXXI, L)
L. VI	,,	,,	,,	3 ×	(Str. dog XVI, LI, LII)
L. VII	,,	,,	,,	6 ×	(Str. dog XVII, XXII, XXIII, XXVI, LIII, LIV)
S. I	,,	,,	,,	2 ×	(Str. dog XXIV, LV).

Some months ago, the researches of **Winkler** and **van Rijnberk** were published,[1] a series of experiments in which, by means of the **Sherrington** isolation method they demonstrated on a large material, comprising 40 objects, the dermatomery of the hindleg in dogs.

When that work was published, the series of my experiments was nearly completed and I could state an indeed striking accordance between the results obtained by those investigators as to shape, situation and extension of the dermatomata they found, and my strychnine segmental zones defined by means of this strychnine method, an accordance and a resemblance that in some cases grew nearly to identity, as will be shown here after.

I intend in the following pages to give the results obtained by me in that respect, comparing everywhere my strychnine segmental zones with the proportions found by **Winkler** and **van Rijnberk** for their dermatomata.

The theoretical speculations and consequences resulting from the facts that will be told, shall not find any place in this communication.

Th. XIII. The strychnine zone of this segment, like those of the trunk segments, presents still a very simple shape, its various properties therefore are clearly enough demonstrated by the Fig. V and VI without adding anything.

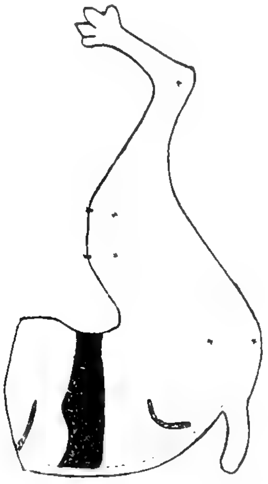

Fig. V. *Th.* XIII.

Fig. VI. *Th.* XIII.

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[1] **Winkler** and **van Rijnberk**. "Experimental researches on the segmental innervation of the skin in dogs". VIth and VIIth communication. These Proceedings of Juny and September 1910.

L. I. What strikes us first of all, is the fact that this strychnine-segmental zone obviously lies more caudalward on the body than the preceding one. To ascertain this, we have only to compare the caudal boundaries of these two zones in their relation to the crista iliaca, as shown resp. in Fig. V and in Fig. VII. Practically this zone is not yet lying on the skin of the extremity, though we may perceive the neighbourhood of this latter by the small linguiform projection presented by this zone in the skinfold of the groin. See Fig. VII. WINKLER and VAN RIJNBERK found analogous proportions for their dermatoma of *L.* I.

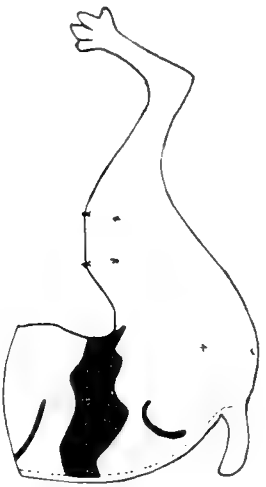

Fig. VII. *L.* I.

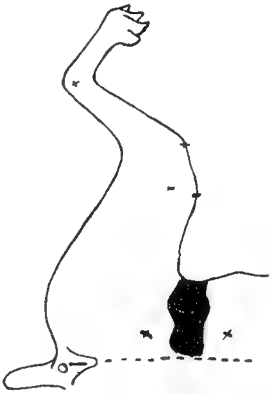

Fig. VIII. *L.* I.

L. II is the first segment, the strychnine-zone of which lies on the skin of the extremity. Compared with the zone of *L.* I it is situated more caudalward, which is shown among others by the fact that the crista ilei now lies partly within this skin-field.

This strychnine-segmental zone extends very far on the lateral surface of the extremity, whilst it covers likewise a great part of its medial surface.

The most distal point of this zone on the extremity is situated at about $2^1/_2$ c.m. from the upper margin of the patella, as is shown in Fig. IX and X. In all my cases the situation of this distal boundary was the same, I also always found the fixed points of the knee-joint lying outside the zone.

The statements of WINKLER and VAN RIJNBERK concerning the dermatoma of *L*II, are perfectly identical with what I found about this zone. At the mid-ventral line the strychnine-segmental-zone is rather small and covers the skin of the root of the penis, without passing on the scrotum.

In female animals the caudal boundary of the zone is situated ± $2^1/_2$ c.m. cranially from the foot of the Mons veneris.

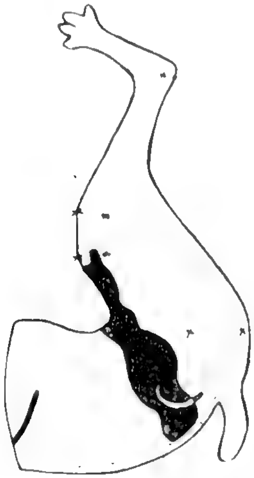

Fig. IX. *L.* II.

Fig. X. *L.* II.

L. III. Contrasting with the nearly for all cases constant situation of the boundaries of the strychnine-segmental zone of *L.* II, as e.g. relative to the trochanter and to the fixed points of the knee-joint, we remark in the zone of *L.* III that, though the form remains nearly the same, the situation of the boundaries in different cases is rather variable.

In Str. dog XLVIII e.g. I found that the caudal boundary runs

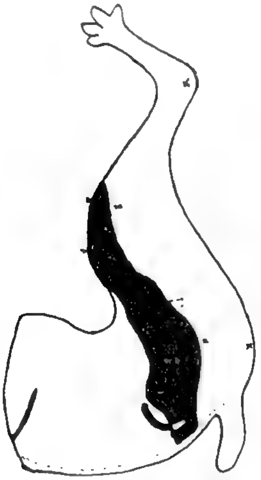

Fig XI. *L.* III.

Fig. XII. *L.* III.

about 2 c.m. cranially from the throchanter along this latter, whilst in Str. dog XXIX this boundary lies somewhat caudally from this point on the lateral surface of the extremity. Winkler and van Rijnberk likewise stated analogous variations for their dermatomata.

At the mid-ventral line this skin-field extends over the root of the penis and part of the scrotum.

L. IV. The strychnine zone of this segment presents a strong likeness to that of the preceding segment, only it is situated more caudalward and therefore farther distally on the extremity.

At the mid-dorsal line the cranial boundary is always found caudally from the crista ilei. On the lateral crural surface the caudal boundary in most cases runs nearly across the trochanter in the direction of the knee-joint and passes the crista tibiae ± 4 c.m. distalward from the tuberositas tibiae.

At the mid-ventral line the scrotal skin is covered by this zone.

Fig. XIII. *L.* IV.

Fig. XIV. *L.* IV.

L. V. It is characteristic for this strychnine-segmental zone that it has lost all connection as well with the mid-dorsal as with the mid-ventral line of the body. Winkler and van Rijnberk likewise found this to be the case for their dermatoma of *L*, V, and for this reason gave it the name of first "top-dermatoma". The zone extends partly over the lateral, for another and greater part over the medial crural surface. Its most proximal point is lying on the lateral crural surface nearly in the middle of the line connecting throchanter and epicondylus femoris lateralis. From this point the cranial boundary goes distalward, passes on the inner surface of the extremity and thence bends to the medial crural surface.

The caudal boundary of this strychnine-segmental zone passes on the medial surface of the nether-leg between the proximal and the medial third of the crista tibiae.

On this portion of the extremity this skin-area lies entirely on the medial side, so that it presents itself here as a narrow tongue, which for different cases differs in its extending more or less far distalward. Sometimes it reaches not farther than the malleolus medialis, in other cases it even joins the sole of the medial toe. The malleolus medialis either lies in the middle of this narrow tongue or just on its cranial boundary.

Analogous proportions were found by WINKLER and VAN RIJNBERK for their dermatomata of *L.* V.

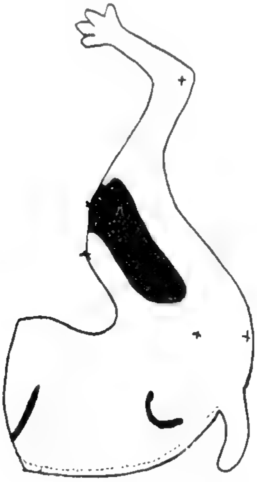

Fig. XV. *L.* V.

Fig XVI. *L.* V.

L. VI. Farther still than the strychnine-segmental-zone of *L.* V that of the VIth lumbar spinal segment is lying on the medial surface of the extremity. Only a very small portion of it is still situated on the lateral surface of the extremity. Whilst the zone of *L.* V covers at the utmost the skin of the medial toe, the strychnine-zone of *L.* VI covers the whole of the medial half of the foot, as well on the palmar as on the dorsal surface. Like WINKLER and VAN RIJNBERK, whose data for the dermatoma of *L.* VI are in accordance with those found by me for the corresponding strychnine-segmental zone, stated for the dermatoma, we may therefore say that the strychnine-zone of *L.* VI appears wound spirally around the netherleg and the foot. In none of my cases I found this zone connected with the midventral or the mid-dorsal line, as little as the authors quoted above, found such a connection for their dermatoma of *L.* VI.

L. VII. The strychnine-zone of this segment likewise lies distally on the extremity, although it extends already much farther proximalward on the lateral surface. This zone presents a typical long-stretched shape, and its situation and extension too are in all cases characteristic.

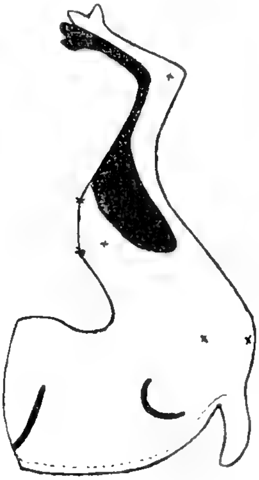
Fig. XVII. *L.* VI.


Fig. XVIII. *L.* VI.

As regards its situation, this skin-zone is characterized by the fact, that it covers the lateral surface of the foot and the netherleg, and extends over a large portion of the postero-lateral surface.

The extension of this strychnine-segmental-zone is a rather variable one. Whilst sometimes these zones extend distalward only to the malleolus lateralis, there may be found others, and such is generally

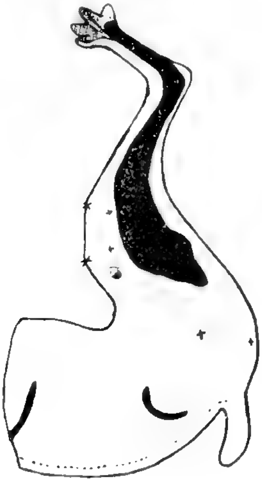
Fig. XIX. *L.* VII.

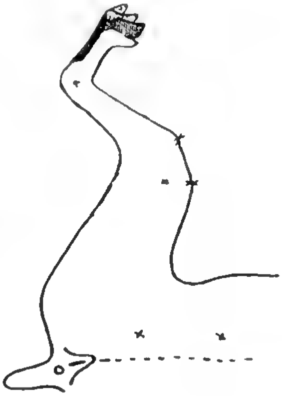
Fig. XX. *L*, VII.

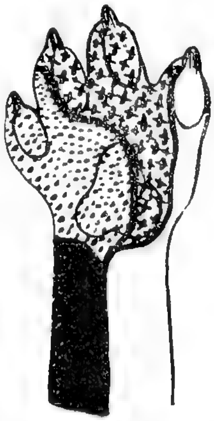
Fig. XXI. *L.* VII.

the case, covering also still a portion of the foot, either only the skin of the lateral toe or the whole of the lateral half of the foot.

WINKLER and VAN RIJNBERK found identical proportions for their dermatomata of *L.* VII. As the average size of this strychnine-segmental-zone I think we may assume that where, both on the dorsum and on the sole of the foot, the skin of the two lateral toes is covered by its area.

Fig. XXI reproduces the divers variations in extension of the *L.*VII zone on the foot as found in my experiments.

S. I. According to the statements of WINKLER and VAN RIJNBERK, the dermatoma of *S* I is the first caudal marginal dermatoma, i.e. the first of the caudal dermatomata of the extremity that has recovered the connection with the mid-dorsal and mid-ventral lines.

The corresponding strychnine-segmental-zone behaves exactly in the same way.

In as much as this zone extends over the proximal portion of the extremity, there is accordingly a fundamental difference between it and the preceding strychnine-segmental-zone. At the distal end of the extremity however the two zones are nearly identical as to shape and extension, though it may be taken for granted that generally the zone of *S* I is situated somewhat more on the posterior surface than that of *L.* VII and does not extend as far distalward as this latter.

For, in as much as I was able to state so from my material, the narrow tongue, protruding from this zone on the nether-leg never extends farther than unto the tuber calcanei.

WINKLER and VAN RIJNBERK, who have isolated in 5 cases the

Fig. XXII. *S* I.

Fig. XXIII. *S* I.

dermatoma of *S*. I, stated in one of these[1]) (dog 11) that here the skin-field extended to the lateral toe. In the four remaining cases the distal boundary of the dermatoma was lying also between fossa poplitea and tuber calcanei.

The strictly localized application of strychnine on the dorsal surface of the first sacral segment presents certain difficulties, not only because this portion of the spinal cord is rather wanting in length, but also, and this latter factor especially gives rise to obstacles, because the dorsal surface of this segment is almost entirely covered by the cauda equina, which is strongly developed in this region of the spinal cord.

Still much worse those difficulties become in the more caudal segments of the sacral spinal cord, in these latter therefore there can be no question of precise localisation, and for this reason I have closed my series of experiments with the definition of the strychnine-segmental-zone of *S* I.

We have now come to a summary of our results.

The first strychnine-segmental-zone lying on the extremity is that of *L* II, for this zone is the first covering the greater part of the skin on the anterior crural surface.

The zones of the segments *L* III and *L* IV resemble one another very closely, and though it cannot be denied that their conformity presents many individual variations, yet in a general way we may conclude that the caudal boundaries of these two strychnine-segmental-zones are nearly identical, and that this common boundary runs along a line, departing from the mid-dorsal line in the middle of the sacrum, and goes over the trochanter in the direction of the epicondylus femoris medialis.

The zone of the segment of *L* V is the first zone of the posterior extremity no longer connected with the mid-ventral and the mid-dorsal lines. WINKLER and VAN RIJNBERK, when stating the same fact for their dermatoma of *L* IV, call it therefore the first top-dermatoma, understanding by this name the dermatomata lying on the apex of the extremity, this latter considered as a cone with an obtuse top.

The strychnine-segmental-zones of *L* VI and *L* VII have likewise lost all connection with the mid-dorsal and mid-ventral lines, whilst that of *S* I is again in coherence with both. These statements are in perfect accordance with those given by WINKLER and VAN RIJNBERK for the corresponding dermatomata, as indeed we have remarked before. When assuming therefore the terminology of those authors,

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[1]) WINKLER and VAN RIJNBERK, VIth Communication. l. c. p. (304) 33.

we may say that on the hind-leg there ought to be distinguished 3 cranial marginalstrychnine-segmental-zones, viz. those of *L* II, *L* III, and *L* IV, 3 apical strychnine-segmental-zones, viz. those of *L* V, *L* VI, and *L* VII, and at least 1 caudal marginal strychnine-segmental zone, viz. that of *S* I.

According to WINKLER and VAN RIJNBERK, the dermatomata of *S* II and *S* III are still caudal marginal dermatomata of the posterior extremity, these two being then the last. As we told before, it is impossible to obtain a strictly localized strychnine-application on these segments, for which reason I have not determined their corresponding strychnine-segmental-zones.

When examining Fig. XXII, we may see that the cranial boundary of the strychnine-segmental-zone of *S* I leaves the mid-dorsal line at the centre of the sacrum and passes over the trochanter, directed towards the epicondylus medialis, changing then its direction somewhat distally from the trochanter and bending to the posterior surface of the extremity.

For the common caudal boundary of the zones of *L* III and *L* IV we could state an identical course, at least unto a point somewhat distally from the trochanter. In this case therefore the strychnine-segmental-zones of segments not immediately succeeding one another in the series are bounded by one another.

WINKLER and VAN RIJNBERK found wholly identical relations for their dermatomata, and design therefore this demarcation-line between skin-fields that originally are not bounded by one another as the "dorsal axis-line" (SHERRINGTON) or the "dorsal differential boundary" (BOLK) of the extremity.

On the ventral side and the medial surface of the posterior extremity we find the following relations:

The caudal boundaries of the strychnine-segmental-zones of *L* II, *L* III, and *L* IV run along the same line for a large part of their course; it may even be said nearly that the ventral portions of these zones entirely cover one another reciprocally.

Although the lack of fixed points on the abdomen and the medial crural surface (the nipples may on no account be regarded as such) is a cause why the course of the zonal boundaries cannot be defined as sharply as on the extremity, yet we make a very near approach to expressing the genuine relations, when saying that the common caudal boundary of the *L* II, *L* III and *L* IV strychnine-zones is formed by a line departing from the symphysis in the direction of a point, situated on the medial surface of the extremity nearly in the middle between epicondylus femoris medialis and fossa poplitea. The caudal boundaries of the *L* III and *L* IV zones even pass over this point and consequently run together over the whole of the medial crural surface, whilst the caudal boundary of *L* II, leaving this line somewhere in its course, diverges thence with the common caudal boundary of the *L* III and *L* IV zones.

The cranial boundary of the strychnine-zone of *S* I, as is clearly shown by Fig. XXIII, likewise leaves the mid-ventral line just before the symphysis, after a short course it bends more caudalward in the direction of the epicondylus femoris medialis, and continues farther, over the point mentioned above that lies in the middle between this epicondylus and the fossa poplitea, in the direction of the malleolus medialis. Evidently here on the medial crural surface too, there is a demarcationline between skinfields that are not originally bounded by one another.

WINKLER and VAN RIJNBERK, in their VIIth communication have stated an identical course for the demarcation-line between the dermatomata of *L*. II, *L*. III, *L*. IV and *S* I, and by them this line is denominated the "ventral axis-line" (SHERRINGTON) or the "ventral differential boundary" (BOLK) of the extremity.

As may be seen from the foregoing, there is a striking accordance between the results of the researches on the dermatomata of those authors, and the facts stated in this communication.

This accordance however goes still farther, for it is shown not only in what may be called "normal" cases 1), but also in such

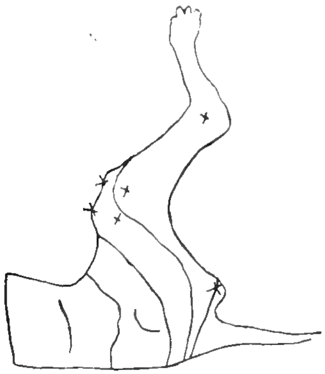

Fig. XXIV.
[Fig. VIII. 1.
L IV. Dog 19. Prefixion of the extremity (after WINKLER and VAN RIJNBERK)].

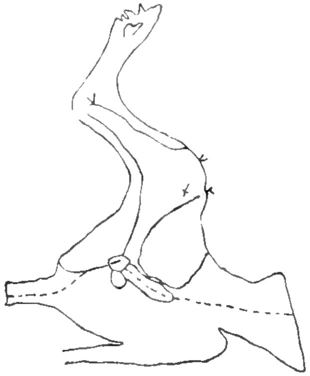

Fig. XXV.
[Fig. VIII. 2.
L IV. Dog 19. Prefixion of the extremity (after WINKLER and VAN RIJNBERK)].

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1) In as much as the term "normal" may be applied to any relations concerning the peripheral skin-innervation. According to the data of WINKLER and VAN RIJNBERK, SHERRINGTON's "prefixed" and "postfixed type" must be considered as extrema

cases where anomalies in the construction of the skeleton of the vertebral column produce alterations in the dermatomery and in shape, situation, and extension of the strychnine-segmental-zones.

Winkler and van Rijnberk in the course of their experiments have met with one case (dog 19), where the dermatoma of *L.* IV presented a shape diverging from the "normal", because in contrast with their other cases of isolation of this skin-area, it sent a narrow linguiform branch on the medial surface of the nether-leg [1]). (Fig. XXIV and XXV).

It was therewith characterized as it were as a transition form between a *L* IV and *L* V dermatoma. At the autopsy the dog was found to possess only 6 lumbar vertebrae, so this presented a case of so-called "prefixion of the extremity" (Sherrington).

In one of my cases (str. dog XIV) where I had applied strychnine on the 4th lumbar segment, I found a zone shaped nearly identically to that observed by Winkler and van Rijnberk in the case of isolation of the *L.* IV dermatoma, described above. See Fig. XXVI and XXVII. This dog was likewise found to possess only 6 lumbar vertebrae.

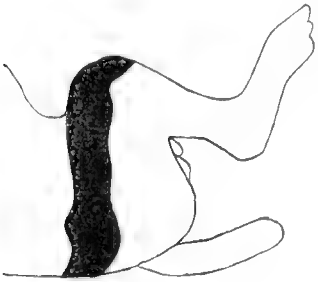

Fig. XXVI.
L. IV. Prefixion of the extremity.

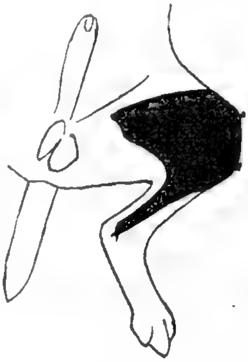

Fig. XXVII.
L. IV. Prefixion of the extremity.

Besides in this respect, this experiment is still interesting in another way.

On page (439) 9 of their VIIth communication the authors repeatedly

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as regards the metamere skin-innervation, so that practically there exist numerous intermediate forms. Among my results I find likewise several data, supporting this conception. But speculations on this point, however interesting and important for the question of the dermatomery, would lead me too far here.

[1]) Winkler and van Rijnberk, VIth communication l.c. page (321) 15. Fig. VIII.

quoted by us, enter in elaborate details about the manner in which the axis-lines [1]) of the extremity behave.

In Fig. XXVIII I give a scheme of the demarcation-line between the strychnine-segmental-zones of *L*II, III, IV, and *S* I, as its course was found to be according to my data, a line, as already stated before, perfectly identical with the dorsal axis-line of the extremity, described by WINKLER and VAN RIJNBERK.

This line ends at the point, lying proximo-lateral on the thigh, which is common to the *L*. V, *L*. VI and *L*. VII zones, whence these zones diverge like the sectors of a fan, largely overlapping one another.

And now the ventral axis-line.

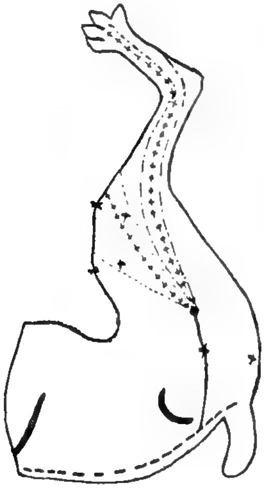

Fig. XXVIII.

——— ⁺ ● = demarcation-line between strychnine-segmental zones of *L*. II, III, IV, and *S* I.

... . = boundary of zone of *L*. V.

+++ — „ „ „ „ *L*. VI.

·.·.·.·.·. = „ „ „ „ *L*. VII.

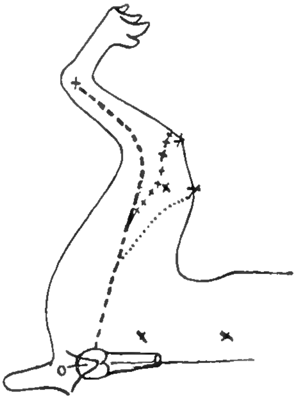

Fig. XXIX.

···· = demarcation-line between strychnine-segmental zones of *L*. II, III, IV, V, and *S* I.

.... = caudal boundary of the zone of *L*. II after the demarcation-line.

+++ = caudal boundary of the zones of *L*. III and IV after the demarcation-line.

Basing their conclusion on their "normal" material, but likewise on the abnormal cases and especially on their case "dog 19",

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[1]) As is well known, SHERRINGTON indicates as the characteristic of his axis lines a functional specific quality, viz. the unimportant measure of the "overlapping" of the dermatomata bounding one another in that region, whilst BOLK for his "differential boundary", which is identical with this axis line, gives a morphological characteristic, indicating as such the demarcation-line between dermatomata originally not lying next to one another, but pushed into each other's neighbourhood by the development of the extremity during its ontogenesis.

WINKLER and RIJNBERK, retaining withal the criteria of the definitions of BOLK and SHERRINGTON, specified as ventral axis-line the line going from the symphysis over the medial surface of the extremity towards the malleolus medialis, passing in its course over the point situated in the middle between epicondylus femoris and fossa poplitea.

Now this line is identical with the demarcation-line between the strychnine-segmental zones of *L* II, *L* III, and *L* IV on one hand and of *S* I on the other, as described in the foregoing.

And this case of my Str. dog XIV gives still further confirmation of that accordance, because it bears testimony (see fig. XXVII) that 1st. in cases of prefixion of the extremity the strychnine-segmentalzones too, like the dermatomata, are removed (apparently) caudalward on the extremity, 2nd. that this removal obviously takes place along the demarcation-line that was proved to be the homologon of the ventral axisline for the dermatomata. (See fig. XXIX).

Still in another respect I may point to analoga, even to identity. In one of their first communications on the dermatomata the authors quoted above have demonstrated that each filum radiculare of a posterior spinalroot contributes to the innervation of the whole dermatoma, founding this statement on the fact, that if from a pair of successive posterior roots either only the cranial or only the caudal fila radicularia were cut through, they never found a zone where sensibility was destroyed, but on the contrary an area, corresponding in extension with the number of posterior roots that were cut through partially, presenting a uniform hyperalgesy.

In the course of my strychnine experiments I met with a similar fact. It is not only the poisoning of the dorsal surface of an entire segment that gives rise to the appearance of the strychnine-zone characteristic for this portion of the spinal cord, but also if the alkaloid is applied on part of it, e.g. on that part where the 2 cranial fila radicularia enter, the strychnine-segmental-zone is seen to appear in toto. And that this zone appears to its whole extent, is proved moreover among others by the fact that it does not increase in size if afterwards the strychnine is applied too on the remaining portion of the dorsal surface of the segment.

Where the accordance existing in shape, situation, and extension between the dermatomata defined by the isolation-method and the strychnine-segmental zones found by this strychnine-method, is so striking, it proves the truth of a presumption that obviously was ours from the beginning, viz. that these strychnine-segmental-zones present skinfields, identical as to the said attributes, shape, situation and extension, with dermatomata.

The facts here stated may lead to various theoretical speculations, important for the physiology of the central nervous system, and in a further communication I hope to be able to develop the theoretical views following from our data, views touching on different questions concerning the morphological foundations of the physiology of the spinal cord, the functions of this organ and of the central nervous system generally.

The conclusions, which I would propose as a summary of the results of these researches, in as much as they concern the special question about shape, situation and extension of the strychnine-segmental zones, are the following:

I. *After segmental application of strychnine on the dorsal surface of the spinal cord the strychnine-syndrome, demonstrated by me, appears in sharply circumscribed skinfields, which are identical, as regards their shape, situation, and extension, with the dermatomata defined by means of the isolation method.*

II. *In this strychnine-method, i. e. the segmental, strictly localized application of strychnine on the dorsal surface of the spinal cord, we have got a new method, fundamentally different from all other hitherto known methods, for the definition of the dermatomery of the body.*

Chemistry. — "*Equilibria in the system: Water — Sodium sulphate — Sodium chloride — Copper sulphate Cupric chloride*".

By Dr. F. A. H. Schreinemakers.

(Communicated in the meeting of March 25, 1911).

1. Introduction.

In a previous communication[1] I discussed the equilibria which occur at 30° in the system: Water — Ammonium sulphate — Ammonium chloride — Copper sulphate-Cupric chloride. I have now replaced the ammonium salts in this system by the corresponding sodium salts. This causes the equilibria to become more complicated, and also their form to be more dependent on the temperature. For this reason I have also investigated this system at different temperatures viz. at 35°, 25° and 15°.

At first sight one might think that the system is built up of five

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[1] These Proceedings XI p. 615.

components; this, however, is not the case because between four of these substances occurs the reaction:

$$Na_2SO_4 + CuCl_2 \rightleftarrows CuSO_4 + Na_2Cl_2,$$

so we are only dealing with a quaternary system in which double decomposition occurs.

In order to represent the equilibria in this system we take a quadrangle; its apexes indicate the four substances $CuSO_4$, $CuCl_2$, Na_2SO_4, and Na_2Cl_2, and in such a manner that the sulphate of the one metal is connected by a diagonal with the chloride of the other metal. In the intersecting point of the diagonals we take, perpendicularly on the quadrangle, the axis on which the water content of the phases is shown.

2. THE ISOTHERM AT 35°.

The equilibria occurring at 35° are represented schematically in fig. 1. The sides of the quadrangle have been left out; only a portion of the diagonals with their intersecting point *W* is drawn. Also, the representation in space of the equilibria is not drawn but their projection on the quadrangle is shown.

We will first consider the four ternary equilibria.

a. The system: water — Na_2SO_4 — NaCl.

At 35°, Na_2SO_4 and NaCl only occur as solid phases. The isotherm therefore consists only of two branches namely of the saturation line of Na_2SO_4 and of that of the NaCl. The first is represented by *ak*, the second by *hk*. Point *a* therefore, represents the solubility of the Na_2SO_4, *h* that of the NaCl in water. The intersecting point *k* is the solution which is saturated with the two salts simultaneously.

b. The system: water — NaCl — $CuCl_2$.

At 35° occur as solid phases: NaCl and $CuCl_2 . 2H_2O$. The isotherm therefore, consists of two branches; *hg* is the saturation line of the NaCl, *fg* that of the $CuCl_2 . 2H_2O$. Point *h*, therefore, represents the solubility of the NaCl, *f* that of the $CuCl_2 . 2H_2O$ in water: *g* is the solution which is in equilibrium with both salts at the same time.

c. The system: water — $CuSO_4$ — $CuCl_2$.

In this system also, only two solid phases occur at 35° namely: $CuSO_4 . 5H_2O$ and $CuCl_2 . 2H_2O$. The saturation lines of these salts are indicated by *de* and *fe*. Solution *e* is saturated with:

$$CuSO_4 . 5H_2O + CuCl_2 . 2H_2O$$

d. The system: water — Na_2SO_4 — $CuSO_4$.

In this system three solid phases occur namely: $CuSO_4 . 5H_2O$, Na_2SO_4 and a double salt $Na_2Cu(SO_4)_2 . 2H_2O$.

The saturation line of the Na_2SO_4 is represented by *ab*, that of the $CuSO_4 . 5H_2O$ by *cd* and that of the double salt by *bc*. Solution *b* is, therefore, saturated with Na_2SO_4 and double salt, solution *c* with $CuSO_4 . 5H_2O$ and double salt.

e. The quaternary system.

In this system occur at 35° as solid phases: NaCl, Na_2SO_4, $CuSO_4 . 5H_2O$, $CuCl_2 . 2H_2O$ and the double salt $Na_2Cu(SO_4)_2 . 2H_2O$.

As the quaternary solutions saturated with a solid substance are represented by a surface in space (the saturation surface) we have five saturation surfaces. Their projections are found in fig. 1.

f g m n e is the saturation surface of $CuCl_2 . 2H_2O$
h g m l k ,, ,, ,, ,, ,, NaCl
a b l k ,, ,, ,, ,, ,, Na_2SO_4
d c n e ,, ,, ,, ,, ,, $CuSO_4 . 5H_2O$
b l m n c ,, ,, ,, ,, ,, $Na_2Cu(SO_4)_2 . 2H_2O$

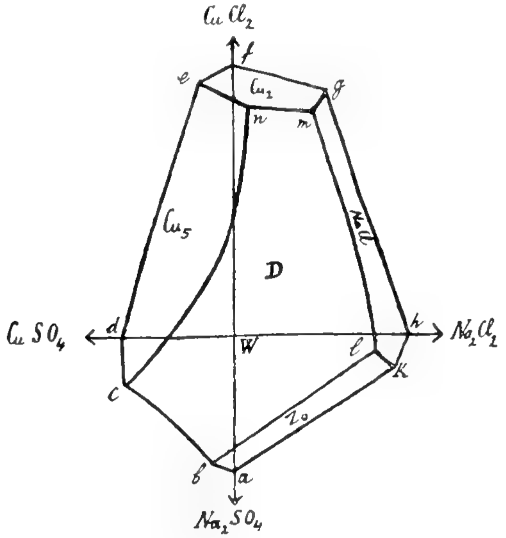

Fig. 1.

In order to obtain a better view, there is indicated in the figure on each saturation surface the solid substance with which the solutions are saturated. By way of abbreviation we have represented

$CuSO_4 . 5H_2O$ by Cu_5, $CuCl_2 . 2H_2O$ by Cu_2, Na_2SO_4 by Z_0 and the double salt $Na_2Cu(SO_4)_2 . 2H_2O$ by D.

The intersecting lines of the saturation surfaces are the saturation lines; these represent the solutions which are saturated with two solid substances simultaneously. The following ones are found:

e n the saturation line of $CuSO_4 . 5H_2O + CuCl_2 . 2H_2O$
n m ,, ,, ,, ,, $CuCl_2 . 2H_2O + Na_2Cu(SO_4)_2 . 2H_2O$
m g ,, ,, ,, ,, $CuCl_2 . 2H_2O + NaCl$
m l ,, ,, ,, ,, $NaCl + Na_2Cu(SO_4)_2 . 2H_2O$
k l ,, ,, ,, ,, $NaCl + Na_2SO_4$
b l ,, ,, ,, ,, $Na_2SO_4 + Na_2Cu(SO_4)_2 . 2H_2O$
c n ,, ,, ,, ,, $CuSO_4 . 5H_2O + Na_2Cu(SO_4)_2 . 2H_2O$

In addition we have three saturation points, namely, points which represent a solution saturated with three solid substances. They are the following:

n saturated with $CuSO_4 . 5H_2O + CuCl_2 . 2H_2O + Na_2Cu(SO_4)_2 . 2H_2O$
m ,, ,, $NaCl + CuCl_2 . 2H_2O + Na_2Cu(SO_4)_2 . 2H_2O$
l ,, ,, $Na_2SO_4 + NaCl + Na_2Cu(SO_4)_2 . 2H_2O$

As may be readily noticed from fig. 1 in presence of solution there can exist

$CuSO_4 . 5H_2O$ by the side of $CuCl_2 . 2H_2O$ or $Na_2Cu(SO_4)_2 . 2H_2O$ but not to NaCl of Na_2SO_4.
$CuCl_2 . 2H_2O$ by the side of $CuSO_4 . 5H_2O$, NaCl or $Na_2Cu(SO_4)_2 . 2H_2O$ but not to Na_2SO_4
NaCl by the side of $CuCl_2 . 2H_2O$, Na_2SO_4 or $Na_2Cu(SO_4)_2 . 2H_2O$ but not to $CuSO_4 . 5H_2O$
Na_2SO_4 by the side of NaCl or $Na_2Cu(SO_4)_2 . 2H_2O$ but not to $CuSO_4 . 5H_2O$ of $CuCl_2 . 2H_2O$
$Na_2Cu(SO_4)_2 . 2H_2O$ can exist by the side of each of the other salts.

In table I are indicated the compositions of different solutions in Mol. $^0/_0$; the double salt $Na_2Cu(SO_4)_2$ $2H_2O$ is represented by *D*.

TABLE I.

Compositions in Mol. $^0/_0$ at 35°.

Point.	H_2O	$CuSO_4$	$CuCl_2$	Na_2SO_4	Na_2Cl_2	Solid phase.
f.	90,311	0	9.689	0	0	$CuCl_2.2H_2O$
e.	90.108	0.592	9.300	0	0	$CuSO_4.5H_2O+CuCl_2.2H_2O$
g.	88.387	0	8.708	0	2.905	$NaCl+CuCl_2.2H_2O$
f.	90.311	0	9.689	0	0	$CuCl_2.2H_2O$

	e.	90.108	0,592	9,300	0	0	$CuSO_4.5H_2O+CuCl_2.2H_2O$
line *e n*		89.795	0.669	9,034	0	0.502	„ + „
	n.	89.482	0.773	8.796	0	0.949	$CuSO_4.5H_2O+CuCl_2.2H_2O+D$
	n.	89.482	0.773	8.796	0	0.949	$CuSO_4.5H_2O+CuCl_2.2H_2O+D$
line *n m.*		89.0 9	0.437	8.705	0	1.789	$CuCl_2.2H_2O+D$
	m.	88.132	0.299	8.486	0	3.083	$CuCl_2.2H_2O+NaCl+D$
	g.	88.387	0	8.708	0	2.905	$NaCl+CuCl_2.2H_2O$
	m.	88.132	0.299	8.486	0	3.083	$NaCl+CuCl_2.2H_2O+D$
	e.	90.108	0.592	9.300	0	0	$CuSO_4.5H_2O+CuCl_2.2H_2O$
	d.	97.079	2.921	0	0	0	$CuSO_4.5H_2O$
	c.	95.590	2.895	0	1.515	0	$CuSO_4.5H_2O+D$
	d.	97.079	2.921	0	0	0	$CuSO_4.5H_2O$
	c.	95.590	2.895	0	1.515	0	$CuSO_4.5H_2O+D$
line *c n.*		95.619	1.566	1.360	1.455	0	„ + „
		95.310	2.336	0.922	0	1.432	„ + „
		92.961	1.213	4.590	0	1.236	„ + „
	n.	89.482	0.773	8.776	0	0.949	$CuCl_2.2H_2O+CuSO_4.5H_2O+D$
	c.	95.590	2.895	0	1.515	0	$CuSO_4.5H_2O+D$
	b.	94.004	0.235	0	5.761	0	Na_2SO_4+D
	a.	94.106	0	0	5.894	0	Na_2SO_4
	b.	94.004	0.235	0	5.761	0	Na_2SO_4+D
	b.	94.004	0.235	0	5.761	0	Na_2SO_4+D
line *b l.*		94.435	0.200	0	4.080	1.285	„ + „
		94.600	0.196	0	2.640	2.564	„ + „
		94.420	0.267	0	1.575	3.738	„ + „
	l.	93.814	0.482	0	0.629	5.065	$NaCl+Na_2SO_4+D$
	a.	94.106	0	0	5.894	0	Na_2SO_4
	k.	94.130	0	0	1.041	4.829	Na_2SO_4+NaCl
	k.	94.130	0	0	1.041	4.829	Na_2SO_4+NaCl
	h.	94.721	0	0	0	5.279	NaCl
	k.	94.130	0	0	1.041	4.829	Na_2SO_4+NaCl
	l.	93.814	0.482	0	0.639	5.065	$Na_2SO_4+NaCl+D$

h.	94.721	0	0	0	5.279	NaCl
g.	88.387	0	8.708	0	2.905	$NaCl + CuCl_2.2H_2O$
l.	93,814	0,482	0	0,639	5,065	$Na_2SO_4 + NaCl + D$
	93,419	0	1,218	0,758	4,605	$NaCl + D$
line *l m.*	93,023	0,550	1,606	0	4,821	„ + „
	92,089	0,445	3,177	0	4,239	„ + „
	91,195	0,389	4,506	0	2,910	„ + „
	89,023	0,311	7,559	0	3.107	„ + „
m.	88,132	0,299	8,486	0	2,083	$CuCl_2.2H_2O + NaCl + D$

When studying the given compositions of the solutions we must remember that these may be expressed in different ways.

Let us take a solution which contains:

$$a \text{ Mol } CuSO_4, \qquad b \text{ Mol } CuCl_2, \qquad c \text{ Mol } Na_2SO_4$$

$$\text{and, therefore, } 100-a-b-c \text{ Mol } H_2O.$$

In consequence of the relation;

$$Na_2SO_4 + CuCl_2 \rightleftarrows CuSO_4 + Na_2Cl_2$$

we may also express the composition as:

$$a + x \text{ Mol } CuSO_4, \qquad b - x \text{ Mol } CuCl_2, \qquad c - x \text{ Mol } Na_2SO_4,$$

$$x \text{ Mol } Na_2Cl_2 \quad \text{and} \quad 100-a-b-c \text{ Mol } H_2O.$$

We notice that, in this manner, the composition of a phase may be expressed in an infinite number of ways.

If $b < c$ and $x = b$, the composition becomes:

$$a + b \text{ Mol } CuSO_4, \qquad c - b \text{ Mol } Na_2SO_4, \qquad b \text{ Mol } Na_2Cl_2$$

$$\text{and} \quad 100-a-b-c \text{ Mol } H_2O.$$

3. THE ISOTHERMS BETWEEN 35° AND 25°.

On lowering the temperature the surfaces and saturation lines of fig. 1 undergo a slight change of form but the isotherm up to about 32.5° retains the shape of fig. 1.

For at 32.5° a new phase appears, the hydrate $Na_2SO_4 . 10\ H_2O$. At this temperature there appears in point a of fig. 1 a new saturation surface which extends on further lowering of the temperature. At 32° it passes through the point b and below this temperature the isotherm assumes a form as indicated in fig. 2. This has been determined at 25°.

4. THE ISOTHERM AT 25°.

(Investigated with Miss W. C. DE BAAT).

The equilibria occurring at 25° are represented in fig. 2; these are distinguished from those in fig. 1 by the appearance of a new saturation surface, namely that of $Na_2SO_4 . 10\,H_2O$. This surface is represented in fig. 2 by *abqp*; for the sake of brevity $Na_2SO . 10H_2O$ is called Z_{10}.

First, we must again consider the four ternary equilibria.

a. The system: water—Na_2SO_4—NaCl.

This system is distinguished at 25° from the same system at 35° by the fact that the hydrate $Na_2SO_4 . 10\,H_2O$ also appears. The isotherm, therefore, consists of 3 branches. *ap* is the saturation line of the $Na_2SO_4 . 10\,H_2O$, *pk* that of the anhydrous Na_2SO_4 and *kh* that of the NaCl.

The solution saturated with $Na_2SO_4 . 10\,H_2O + Na_2SO_4$ is, therefore, represented by *p* and the solution saturated with Na_2SO_4 + NaCl by *k*.

b. The quaternary system.

As will be seen at once from a comparison of figs. 1 and 2, the equilibria in the systems water—NaCl—$CuCl_2$, water—$CuSO_4$—$CuCl_2$ and water—$CuSO_4$—Na_2SO_4 at 25° and at 35° belong to the same type.

In the system: water—$CuSO_4$—Na_2SO_4 there is however, one point of difference, namely that branch *ab* indicates, at 35°, the solutions saturated with Na_2SO_4 whereas branch *ab* is, at 25°, the saturation line of the $Na_2SO_4 . 10\,H_2O$.

c. The quaternary system.

In fig. 2 are found the following saturation surfaces:

fenmg,	the	saturation	surface	of	$CuCl_2 . 2\,H_2O$
hgmlk,	,,	,,	,,	,,	NaCl
klqp,	,,	,,	,,	,,	Na_2SO_4
abqp,	,,	,,	,,	,,	$Na_2SO_4 . 10\,H_2O$
dene,	,,	,,	,,	,,	$CuSO_4 . 5\,H_2O$
bcnmlqb,	,,	,,	,,	,,	$Na_2Cu\,(SO_4)_2 . 2H_2O$

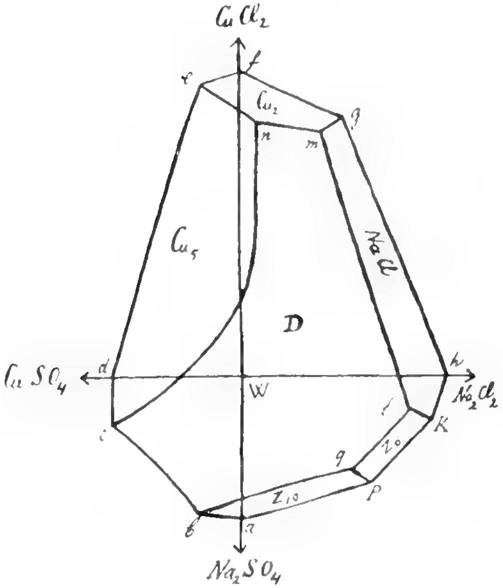

Fig. 2.

Further we have the following saturation lines:

en the saturation line of $CuSO_4 . 5 H_2O + CuCl_2 . 2H_2O$
nm ,, ,, ,, ,, $CuCl_2 . 2 H_2O + Na_2Cu (SO_4)_2 . 2 H_2O$
ml ,, ,, ,, ,, $NaCl + Na_2Cu (SO_4)_2 . 2 H_2O$
mg ,, ,, ,, ,, $CuCl_2 . 2 H_2O + NaCl$
lk ,, ,, ,, ,, $NaCl + Na_2SO_4$
lq ,, ,, ,, ,, $Na_2SO_4 + Na_2Cu (SO_4)_2 . 2 H_2O$
qp ,, ,, ,, ,, $Na_2SO_4 + Na_2SO_4 . 10 H_2O$
qb ,, ,, ,, ,, $Na_2SO_4 . 10 H_2O + Na_2Cu (SO_4)_2 2 H_2O$
cn ,, ,, ,, ,, $CuSO_4 . 5 H_2O + Na_2Cu (SO_4)_2 . 2 H_2O$

Instead of three saturation points as at 35°, four are found here namely:

n saturated with $CuCl_2 . 2 H_2O + CuSO_4 . 5 H_2O + Na_2Cu(SO_4)_2 . 2 H_2O$
m ,, ,, $CuCl_2 . 2 H_2O + NaCl + Na_2Cu (SO_4)_2 . 2 H_2O$
l ,, ,, $NaCl + Na_2SO_4 + NaCu (SO_4)_2 . 2 H_2O$
q ,, ,, $Na_2SO_4 + Na_2SO_4 . 10 H_2O + Na_2Cu (SO_4)_2 . 2 H_2O$

As may be readily deduced from fig. 2, at 25°, in presence of solution there can exist:

$CuSO_4 . 5 H_2O$ by the side of $CuCl_2 . 2 H_2O$ or $Na_2Cu (SO_4)_2 . 2 H_2O$
but not to NaCl, Na_2SO_4 or $Na_2SO_4 . 10 H_2O$.

$CuCl_2 . 2 H_2O$ by the side of $CuSO_4 . 5 H_2O$, NaCl or $Na_2Cu (SO_4)_2 . 2 H_2O$
but not to Na_2SO_4 or $Na_2SO_4 . 10 H_2O$.

NaCl by the side of $CuCl_2 . 2 H_2O$, Na_2SO_4 or $Na_2Cu(SO_4)_2 . 2 H_2O$ but not to $CuSO_4 . 5 H_2O$ or $Na_2SO_4 . 10 H_2O$

Na_2SO_4 by the side of NaCl, $Na_2SO_4 . 10 H_2O$ or $Na_2Cu(SO_4)_2 . 2 H_2O$ but not to $CuSO_4 . 5 H_2O$ or $CuCl_2 . 2 H_2O$

$Na_2SO_4 . 10 H_2O$ by the side of Na_2SO_4 or $Na_2Cu(SO_4)_2 . 2 H_2O$ but not to NaCl, $CuCl_2 . 2 H_2O$ or $Na_2Cu(SO_4)_2 . 2 H_2O$

$Na_2Cu(SO_4)_2 . 2 H_2O$ by the side of all other solid substances.

In table II are given the compositions of the solutions in mol. %.

TABLE II.

Compositions in mol. % at 25°.

Point.	H_2O	$CuSO_4$	$CuCl_2$	Na_2SO_4	Na_2Cl_2	Solid phase.
f.	90,695	0	9,305	0	0	$CuCl_2.2H_2O$
e.	90,534	0,424	9,042	0	0	$CuCl_2 2H_2O+CuSO_4.5H_2O$
f.	90,695	0	9,305	0	0	$CuCl_2.2H_2O$
g.	89,014	0	8,193	0	2,793	$CuCl_2.2H_2O$+NaCl
g.	89,014	0	8,193	0	2,793	$CuCl_2.2H_2O$+NaCl
m.	88,922	0,284	7,994	0	2,800	$CuCl_2.2H_2O$+NaCl+D
e.	90,534	0,424	9,042	0	0	$CuCl_2.2H_2O+CuSO_4.5H_2O$
line *e n*	90,210	0,502	8,692	0	0,596	„ + „
n.	89,760	0,587	8,428	0	1,225	$CuCl_2.2H_2O+CuSO_4.5H_2O$+D
n.	89,760	0,587	8,428	0	1,225	$CuCl_2.2H_2O+CuSO_4.5H_2O$+D
line *n m.*	89,733	0,392	8,271	0	1,604	$CuCl_2.2H_2O$+D
m.	88,922	0,284	7,994	0	2,800	$CuCl_2.2H_2O$+NaCl+D
g.	89,014	0	8,193	0	2,793	$CuCl_2.2H_2O$+NaCl
h.	94,075	0	0	0	5,25	NaCl
m.	88,922	0,284	7,994	0	2,800	$CuCl_2.2H_2O$+NaCl+D
	89,840	0,299	6,651	0	3,210	NaCl+D
	90,700	0,353	5,510	0	3.437	„ + „
	90,851	0,352	5,314	0	3,483	„ + „
	91,371	0,386	4,391	0	3,852	„ + „
	92,222	0,423	3,234	0	4,121	„ + „
line *lm.*	92,924	0,491	2,126	0	4,459	„ + „
	93,362	0	1,839	0,573	4,226	„ + „

	93,779	0	1,167	0,621	4,433	„ + „
	93,939	0	0,582	0,964	4,515	„ + „
	93,857	0	0,474	1,082	4,587	„ + „
	93,862	0	0,377	1,239	4,522	„ + „
l.	93,840	0	0,371	1,269	4,520	$NaCl+D+Na_2SO_4$
h.	94,75	0	0	0	5,25	$NaCl$
k.	94.122	0	0	1,163	4,715	$NaCl+Na_2SO_4$
k.	94.122	0	0	1,163	4,715	$NaCl+Na_2SO_4$
p.	94,60	0	0	2,57	2,83	$Na_2SO_4.10H_2O+Na_2SO_4$
p.	94,60	0	0	2,57	2,83	$Na_2SO_4.10H_2O+Na_2SO_4$
a.	96,57	0	0	3,43	0	$Na_2SO_4.10H_2O$
k.	94.122	0	0	1,163	4,715	$NaCl+Na_2SO_4$
l.	93,840	0	0,371	1,269	4,520	$NaCl+Na_2SO_4+D$
p.	94,60	0	0	2,57	2,83	$Na_2SO_4.10H_2O+Na_2SO_4$
q.	94.444	0.184	0	2,546	2,826	$Na_2SO_4.10H_2O+Na_2SO_4+D$
l.	93,840	0,371	0	0,898	4,891	$NaCl+Na_2SO_4+D$
line *lq.*	93,984	0,355	0	0,955	4,742	Na_2SO_4+D
	94.198	0,251	0	1,483	4,058	„ + „
	94.468	0,200	0	2.101	3,231	„ + „
q.	94,444	0,184	0	2,546	2,826	$Na_2SO_4.10H_2O+Na_2SO_4+D$
a.	96,57	0	0	3,43	0	$Na_2SO_4.10H_2O$
b.	95,525	0,934	0	3,541	0	$Na_2SO_4.10H_2O+D$
b.	95,525	0,934	0	3,541	0	$Na_2SO_4.10H_2O+D$
line *bq.*	95,569	0,680	0	3,234	0,517	„ + „
	95,515	0,580	0	3,069	0,836	„ + „
	95,311	0,394	0	2,793	1,502	„ + „
q.	94,444	0,184	0	2,546	2,826	$Na_2SO_4+Na_2SO_4.10H_2O+D$
b.	95,525	0,934	0	3,541	0	$Na_2SO_4.10H_2O+D$
c.	95,641	2,519	0	1,840	0	$CuSO_4.5H_2O+D$
c.	95,641	2,519	0	1,840	0	$CuSO_4.5H_2O+D$
d.	97,546	2,454	0	0	0	$CuSO_4.5H_2O$

line *cn.*	95,641	2,519	0	1,840	0	$CuSO_4.5H_2O+D$
	95,805	1,024	1,446	1,726	0	„ + „
	94,659	1,406	2,313	0	1,622	„ + „
	93,596	1,063	3,804	0	1,537	„ + „
	91,744	0,909	7,847	0	1,500	„ + „
	91,037	0,682	7,083	0	1,198	„ + „
n.	89.760	0,587	8 428	0	1,225	$CuCl_2.2H_2O+CuSO_4.5H_2O+D$
d.	97.546	2,454	0	0	0	$CuSO_4.5H_2O$
e.	90,534	0,424	9,042	0	0	$CuCl_2.2H_2O+CuSO_4.5H_2O$
surface *D*	96,405	0,687	0	2,509	0,399	D
	95.574	0,664	0	2.960	0,802	„
	94,699	0	1,831	0,852	2,618	„
	93.078	0,603	3,589	0	2,730	„

5. *The isotherms between* 25° *and* 15°.

On decrease of temperature the isotherm at first retains a form as in fig. 2; the points *b* and *c* however approach each other, also the points *p* and *k*, and the points *q* and *l*.

At 17,9° the points *p* and *k* coincide causing the saturation line *pk* of the anhydrous Na_2SO_4 to disappear. The quadrangle (of course with curved sides) is then reduced to a triangle with the apexes *q*, *l* and the point at which *p* and *k* coincide. On further decrease of temperature this triangle gets smaller and disappears at 17.4° in a point. The solution represented by this point is saturated with four solid substances; if we also include the vapour there are six phases in equilibrium, so that we have a sextuple point.

As four components are present in six phases, this system is nonvariant.

These phases are:

$$Na_2SO_4 + Na_2SO_4 \,.\, 10H_2O + NaCl + Na_2Cu(SO_4)_2 \,.\, 2H_2O$$
$$+ \text{solution} + \text{vapour}$$

Below 17°.4 the saturation surface of the Na_2SO_4 therefore, disappears and the saturation surface of the $Na_2SO_4 \,.\, 10H_2O$ borders on that of the NaCl.

On further decrease of temperature the points *b* and *c* rapidly move towards each other; at 16°.7 they coincide. Below this temperature the double salt $Na_2Cu(SO_4)_2 \,.\, 2H_2O$ therefore disappears from the ternary system: water—Na_2SO_4—$CuSO_4$. The double salt then still exists only in quaternary solutions; the isotherm then assumes a form as in fig. 3.

6. *The isotherm at* 15°.

The equilibria occurring at 15° are represented in fig. 3; this is at once distinguished from that at 25° (fig. 2) by the disappearance of the saturation surface Z_0 and because the saturation surfaces of $CuSO_4 . 5H_2O$ and $Na_2SO_4 . 10H_2O$ are partly joined along the line *tu*. The equilibria in the ternary systems water—NaCl—$CuCl_2$ and water—$CuSO_4$—$CuCl_2$ still belong, at 15°, to the same type as at 25° and 35°; these need not, therefore, be discussed any further. The equilibria in the two other ternary systems are however, at 15°, different from what they are at 25° and 35°; we will, therefore, briefly discuss these first.

a. The system water — Na_2SO_4 — NaCl.

At 15°, only $Na_2SO_4 . 10 H_2O$ and NaCl occur as solid substances; the point *r* is, therefore, the solution saturated with $Na_2SO_4 . 10 H_2O + NaCl$. The saturation line of the NaCl is represented by *hr*, that of the $Na_2SO_4 . 10 H_2O$ by *ar*.

b. The system water — $CuSO_4$ — Na_2SO_4.

Owing to the disappearance of the double salt $Na_2Cu (SO_4)_2 . 2 H_2O$ the isotherm consists only of the saturation line *at* of the $Na_2SO_4 . 10 H_2O$ and of the saturation line *dt* of the $CuSO_4 . 5 H_2O$. Solution *t* is saturated with both salts.

c. The quaternary system.

The following saturation surfaces are found:

fenmq the saturation surface of $CuCl_2 . 2 H_2O$
hqmsr ,, ,, ,, ,, NaCl
atusr ,, ,, ,, ,, $Na_2SO_4 . 10 H_2O$
dtune ,, ,, ,, ,, $CuSO_4 . 5 H_2O$
usmn ,, ,, ,, ,, $Na_2Cu (SO_4) . 2 H_2O$

Further, we find the saturation lines:

en the saturation line of $CuCl_2 . 2 H_2O + CuSO_4 . 5 H_2O$
nm ,, ,, ,, ,, $CuCl_2 . 2 H_2O + Na_2Cu (SO_4)_2 . 2H_2O$
mq ,, ,, ,, ,, $CuCl_2 . 2 H_2O + NaCl$

ms ,, ,, ,, ,, $NaCl + Na_2Cu(SO_4)_2 . 2 H_2O$
sr ,, ,, ,, ,, $NaCl + Na_2SO_4 . 10 H_2O$
su ,, ,, ,, ,, $Na_2SO_4 . 10 H_2O + Na_2Cu(SO_4)_2 . 2 H_2O$
un ,, ,, ,, ,, $CuSO_4 . 5 H_2O + Na_2Cu(SO_4)_2 . 2 H_2O$
tu ,, ,, ,, ,, $CuSO_4 . 5 H_2O + Na_2SO_4 . 10 H_2O$.

We also find four saturation points:

n saturated with $CuSO_4 . 5H_2O + CuCl_2 . 2H_2O + Na_2Cu(SO_4)_2 . 2H_2O$
m ,, ,, $CuCl_2 . 2H_2O + NaCl + Na_2Cu(SO_4)_2 . 2H_2O$
s ,, ,, $NaCl + Na_2SO_4 . 10H_2O + Na_2Cu(SO_4)_2 . 2H_2O$
u ,, ,, $CuSO_4 . 5H_2O + Na_2SO_4 . 10H_2O + Na_2Cu(SO_4)_2 2H_2O$.

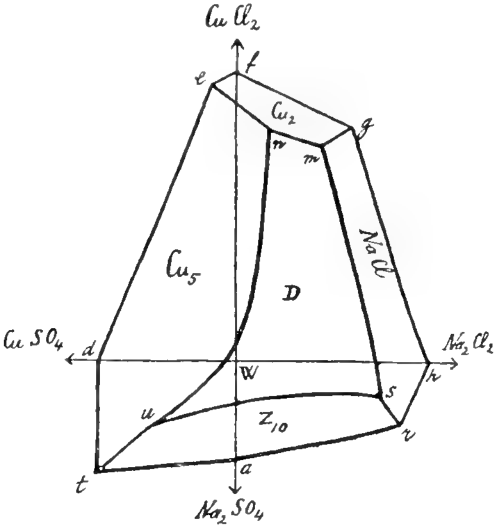

Fig 3.

As will be readily seen from fig. 3, at 15°, in presence of solution there can exist:

$CuCl_2 . 2 H_2O$ by the side of $CuSO_4 . 5 H_2O$, NaCl or $Na_2Cu(SO_4)_2 . 2H_2O$ but not to $Na_2SO_4 . 10 H_2O$;

$CuSO_4 . 5H_2O$ by the side of $CuCl_2 . 2 H_2O$, $Na_2SO_4 . 10H_2O$ or $Na_2Cu(SO_4)_2 . 2H_2O$ but not to NaCl;

NaCl by the side of $CuCl_2 . 2 H_2O$, $Na_2SO_4 . 10 H_2O$ or $Na_2(SO_4)_2 . 2 H_2O$ but not to $Cu SO_4 . 5 H_2O$;

$Na_2SO_4 . 10 H_2O$ by the side of $Cu SO_4 . 5 H_2O$, NaCl or $Na_2 Cu(SO_4)_2 . 2 H_2O$ but not to $CuCl_2 . 2 H_2O$;

$Na_2Cu(SO_4)_2 . 2 H_2O$ by the side of all other solid substances.

In table III are given the compositions of the solutions.

TABLE III.

Compositions in Mol. % at 15°.

Point.	H_2O	$CuSO_4$	$CuCl_2$	Na_2SO_4	Na_2Cl_2	Solid phase.
f.	91,066	0	8,934	0	0	$CuCl_2.2H_2O$
e.	91,020	0,231	8,749	0	0	$CuCl_2.2H_2O+CuSO_4.5H_2O$
f.	91,066	0	8,934	0	0	$CuCl_2.2H_2O$
g.	89,519	0	7,888	0	2,593	$CuCl_2.2H_2O+NaCl$
e.	91,020	0,231	8,749	0	0	$CuCl_2.2H_2O+CuSO_4.5H_2O$
n.	90,023	0,455	7,959	0	1,563	$CuCl_2.2H_2O+CuSO_4.5H_2O+D$
g.	89,519	0	7,888	0	2,593	$CuCl_2.2H_2O+NaCl$
m.	89,509	0,259	7,661	0	2,571	$CuCl_2.2H_2O+NaCl+D$
n.	90,023	0,455	7,959	0	1,563	$CuCl_2.2H_2O+CuSO_4.5H_2O+D$
m.	89,509	0,259	7,661	0	2,571	$CuCl_2.2H_2O+NaCl+D$
g.	89,519	0	7,888	0	2,593	$CuCl_2.2H_2O+NaCl$
h.	94.78	0	0	0	5.22	NaCl
m.	89,509	0,259	7,661	0	2,571	$CuCl_2.2H_2O+NaCl+D$
line *m s.*	92.420	0.439	3.157	0	3.984	NaCl+D
	93,448	0,557	1,164	0	4,831	„ + „
	93,880	0,738	0,312	0	5,070	„ + „
s.	93,947	0,494	0	0,595	4,964	$Na_2SO_4.10H_2O+NaCl+D$
h.	94,78	0	0	0	5,22	NaCl
r.	94,26	0	0	0,95	4,79	$Na_2SO_4.10H_2O+NaCl$
s.	93,947	0,494	0	0,595	4,964	$Na_2SO_4.10H_2O+NaCl+D$
r.	94,26	0	0	0,95	4,79	$Na_2SO_4.10H_2O+NaCl$
r.	94,26	0	0	0,95	4,79	$Na_2SO_4.10H_2O+NaCl$
a.	98,36	0	0	1,64	0	$Na_2SO_4.10H_2O$
s.	93,947	0,494	0	0,595	4,964	$Na_2SO_4.10H_2O+NaCl+D$
line *s u.*	94,676	0,711	0	0,365	4,248	$Na_2SO_4.10H_2O+D$
	95,229	0,948	0	0,251	3,572	„ + „
	95,763	1,282	0	0,400	2,555	„ + „
	95,924	1,839	0	0,987	1,250	„ + „
u.	95,901	2,038	0	1,094	0,967	$CuSO_4.5H_2O+Na_2SO_4.10H_2O+D$

	a.	98,36	0	0	1,64	0	$Na_2SO_4.10H_2O$
	t.	95,83	2,24	0	1,93	0	$Na_2SO_4.10H_2O+CuSO_4.5H_2O$
line *t u.*	*t.*	95,83	2,24	0	1,93	0	$Na_2SO_4.10H_2O+CuSO_4.5H_2O$
		95,861	2,099	0	1,502	0.538	„ + „
	u.	95,901	2,038	0	1,094	0,967	$Na_2SO_4.10H_2O+CuSO_4.5H_2O+D$
	t.	95,83	2,24	0	1,93	0	$Na_2SO_4.10H_2O+CuSO_4.5H_2O$
	d.	97 89	2,11	0	0	0	$CuSO_4.5H_2O$
line *u n.*	*u.*	95,901	2,038	0	1,094	0,967	$Na_2SO_4.10H_2O+CuSO_4.5H_2O+D$
		95,572	2,032	0,277	0	2.119	$CuSO_4.5H_2O+D$
		94,701	1,158	2,137	0	2,004	„ + „
		94,433	1,060	2,533	0	1,974	„ + „
		93.166	0,773	4.192	0	1,869	„ + „
		92,056	0,598	5,628	0	1,718	„ + „
		91,118	0,523	6,652	0	1,707	„ + „
	n.	90,023	0,455	7,959	0	1,563	$CuCl_2.2H_2O+CuSO_4.5H_2O+D$
	d.	97,89	2,11	0	0	0	$CuSO_4.5H_2O$
	e.	91,020	0,231	8,749	0	0	$CuCl_2.2H_2O+CuSO_4.5H_2O$
surface	*D.*	93,365	0,624	3,325	0	2,681	D

In most cases the appertaining residues at 15°, 25°, and 35° have been analysed as well as the solutions, and the solid phases with which the solutions were saturated have been deduced therefrom by means of the usual method.

(*To be continued*).

Chemistry. — "*Hypaphorine and the relation of this substance with tryptophane*". By Prof. P. VAN ROMBURGH.

(Communicated in the meeting of March, 25, 1911).

In the seeds of Erythrina Hypaphorus Boerl. (Hypaphorus subumbrans HASSK.) which, under the name of "dadap minjak" is generally cultivated, in Eastern Java, as a shading tree in coffee gardens, GRESHOFF [1]) has found a poisonous alkaloid.

In the end of 1891 Dr. GRESHOFF had invited me to take in hand, jointly, the study of this alkaloid in order to determine its structure. Shortly afterwards Dr. GRESHOFF was obliged, in the course of 1892, to return to Europe. In the beginning of 1892 I

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[1]) Mededeelingen uit 's Lands Plantentuin **7**, 29 (1890).

was engaged for some time on the investigation of the "dadap substance", but suspended the work after his departure from Java.

In 1898 appeared a communication [1]) on hypaphorine, the name meanwhile given to the substance obtained from the "dadap seeds", from the hand of Dr. GRESHOFF, in which, however, the results obtained by myself, were not included.

In that communication are given the method of preparation of hypaphorine and also its properties.

As regards its properties it may be mentioned here that hypaphorine crystallises in hydrated transparent crystals, which effloresce in a desiccator. At 255° it melts without decomposition. On being heated strongly in the air it burns with evolution of vapours having an odour resembling indol. It has a right-handed rotation $[\alpha]_D = +91° - 93°$. Although hypaphorine possesses a neutral reaction, it yields with acids crystallised compounds of which the sparingly soluble nitrate is particularly characteristic. No formula could be deduced from the recorded analyses of the hypaphorine and its nitrate. In the "Index Phytochemicus" by RITSEMA and SACK, published in 1905, the formula $C_{14}H_{18}N_2O_2$ is, however, given for hypaphorine, but without any mention being made of the source.

After the decease of Dr. GRESHOFF, I applied to the Committee of the Colonial Museum at Haarlem with the request to forward me the preparations of hypaphorine from the laboratory of the Museum in order to enable me to continue the investigation, started previously at Buitenzorg. I have to tender my sincere thanks to that Committee for the great willingness with which, a few months ago, my request was complied with.

The elementary analysis of the anhydrous hypaphorine gave me, at Buitenzorg, the following results:

C 68.4 ; 68.4. H 7.68 ; 7.63. N 10.9 ; 11.—.

Calculated for $C_{14}H_{18}N_2O_2$: C 68.24, H 7.38, N 11.37.

The hydrochloride gave: 13.1 % ; 13.1 % HCl.

Calculated for $C_{14}H_{18}N_2O_2 . HCl$: 12.95 % HCl.

On heating with strong aqueous potassium hydroxide, hypaphorine is decomposed. A gas having an amine-like odour is evolved and the aqueous distillate contains oily drops, which solidify after a while. The gas evolved was collected in dilute hydrochloric acid and the solid matter was separated by filtration from the aqueous distillate. The aqueous solution was united with the hydrochloric acid in which the said amine had been absorbed and evaporated. From the brown

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[1]) Mededeelingen uit 's Lands Plantentuin **25**, 54 (1898).

coloured salt the amine was then again liberated, combined with hydrochloric acid and converted into the platinum chloride compound, which was analysed.

Found 36.8% Pt., the calculated percentage for $[(CH)_3N.HCl]_2PtCl_4$ being 36.94. The amine found is, therefore, trimethylamine.

The substance distilled over with the water, had a strong faecal odour and melted at 52°. It contains nitrogen.

Analysis: Found: C 82.2 H 6.24 N 11.72.

Calculated for C_8H_7N : C 82.-, H 6.04, N 11.96.

With s. trinitrobenzene it yields an additive compound m. p. 187° crystallising in golden yellow needles; it proved to be identical with a product formed from indol and s. trinitrobenzene[1]).

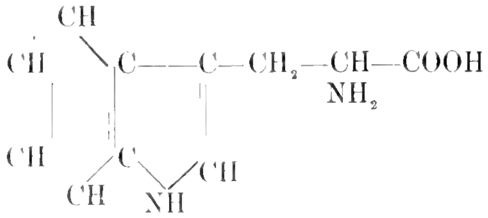
During the action of potassium hydroxide indol as well as trimethylamine has, therefore, been formed.

The behaviour of hypaphorine towards nitric acid pointed to its being a urea derivative, but this view could now no longer be entertained.

Experiments, intended to elucidate the structure, carried out in my laboratory by Mr. Holtappel and consisting in the oxidation of hypaphorine with potassium permanganate and sulphuric acid, or with hydrogen peroxide in either neutral or alkaline solution led to no result except that the formation of trimethylamine could be demonstrated. Heating with hydrochloric acid, which caused charring, did not yield the desired result either. Oxidation experiments with ferric chloride are still in progress.

From the decomposition with potassium hydroxide in which indol and trimethylamine were obtained and which had rendered it probable that hypaphorine is a betaïne, one feels inclined to look upon it as being derived from an amino acid belonging to the indol series and having the formula $C_{11}H_{12}N_2O_2$.

Among the acids which satisfy that condition we find mentioned in Richter's Lexikon (Suppl. III) tryptophane to which belongs, according to Ellinger's[2]) synthesis, the structural formula:



Through the great kindness of our fellow member Prof. Pekelharing, to whom I feel very grateful for this, I had come into possession

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[1]) R. **14**, 66 (1895).

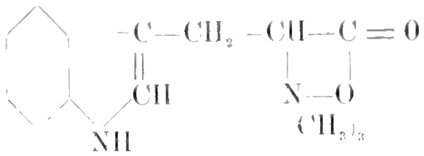
[2]) B. **40**, 3029 [1907].

of 0.2 gram of tryptophane. This, according to the classic method of PETER GRIESS [1]), was mixed in methyl alcohol solution with sodium hydroxide and an excess of methyl iodide. After a few hours, the alcohol and the excess of methyl iodide were removed by distillation in a waterbath. If now the residue is taken up with a little water and mixed with dilute nitric acid a nitrate crystallises in delicate needles when the sides of the beaker are rubbed with a glass rod. I obtained about 0.12 gram of the nitrate.

The nitrate exhibits in its reactions the greatest resemblance with the nitrate of hypaphorine. Like the latter it has no sharp melting point; at about 220° the two preparations contained in capillary tubes were converted amid effervescence into a black mass. This decomposition point depends on the manner of heating.

On boiling with aqueous potassium hydroxide the synthetic nitrate also yields vapours having an odour of amine and indol [2]).

From the experiments described we may draw the conclusion that it is highly probable, that hypaphorine is identical with α-trimethyl-β indolpropio-betaïne:



derived from tryptophane.

In order to get perfect certainty and also to be able to perform the required analyses, I intended to carry out the synthesis of this betaïne on a larger scale, when last week I received from Dr. BARGER in London a letter communicating that by methylating tryptophane according to ENGELAND [3]) and treating the product formed in this reaction with dilute aqueous potassium hydroxide, he had obtained a betaïne, the nitrate of which has the same properties as that of hypaphorine. A determination of the rotatory power could be made. Found $[\alpha]_D = +94°$ whereas GRESHOFF states $+91—93°$.

In consequence, I limit myself to the short, preliminary communication of my results and intend to return to the synthesis, jointly with Dr. BARGER.

Utrecht. *Org. Chem. Lab. University.*

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[1]) B. 8, 1406 [1875].

[2]) Tryptophane when boiled with strong aqueous potassium hydroxide certainly yields a distillate which gives with HNO_2 the indol reaction, but with hypaphorine the splitting takes place much more easily, which fact is not readily accounted for by the formula

[3]) B. 42, 2962 [1909]; 43, 2662 [1910].

Physiology. — "*A new method of determining the arterial blood-pressure in man; at the same time an attempt at estimating the influence of the arterial wall on it*". By Dr. D. DE VRIES REILINGH. (Communicated by Prof. WENCKEBACH).

(Communicated in the meeting of March 25, 1911).

I. A SHORT SURVEY OF THE USUAL METHODS.

The arterial blood-pressure in man was in the beginning determined according to the older methods of VON BASCH, VON FREY, POTAIN, and others. By these methods, as the newer methods of investigation teach us, only an approximate estimation was obtained.

A great improvement in the solution of the problem was obtained by the invention of RIVA-ROCCI and HILL and BARNARD i.e. by the method of the circular compression of the arm by a hollow rubber armlet in which the pressure could be increased and diminished. Originally only a narrow armlet was used, but VON RECKLINGHAUSEN showed that the influence of the surrounding tissues of the arm was considerably less, if an armlet of at least 13 c.m. broad was used. Since that time this broad armlet is almost universally used. LEONARD HILL even makes the determinations of the blood-pressure with an armlet of 20 cm. broad.

Now the blood-pressure is usually measured according to two different principles, according to which it is customary to distinguish the oscillatory and the palpatory method.

A. Oscillatory method.

A hollow armlet is applied to the upper-arm of the person that is to be examined, whilst the pressure of air in the interior of the armlet is constantly increased. Then there occur in the armlet pulsations, the intensity of which can be determined in some way or other: either by registering them graphically on a revolving drum or by reading them from a mercury- or water-column or any other index connected with the armlet.

The peculiarity of these pulsations is that they increase in the same measure as the pressure in the armlet increases, till they have reached a certain maximum, and that afterwards, when the pressure in the armlet augments, they decrease and disappear at last almost entirely.

Originally it was admitted, that the diastolic or minimal blood-pressure (*mBp*) in the armlet was reached when it showed the greatest pulsations. It was supposed that just then the artery during the diastole was completely closed by the pressure of the armlet, but that it could expand itself still fully during the systole of the heart, so that, at that moment, the differences in width of the artery during the two phases of the heart were greatest.

And the current view was that the systolic or maximal blood-pressure (*MBp*) in the armlet was reached when the latter showed no longer any or hardly any pulsations. It was admitted that then the artery, likewise during the systole of the heart, was tightly compressed by the armlet, so that it could no longer transfer pulsations to the armlet.

Both these theories are objectionable.

In the first place the investigators very soon held different views about the pulsations of the air in the armlet that indicated that the *mBp* was reached. Originally they were inclined to suppose that at the moment, when the maximal pulsations were observed, there was *mBp* in the armlet. Afterwards they thought that the *mBp* in the armlet was reached, when the pulsations in it at increasing pressure began to become greater. The pressure of the armlet was thought to be at that moment just a little greater than the diastolic pressure in the artery. Consequently this artery would be a little compressed during the diastole of the heart. From this moment therefore the fluctuations of volume in the artery would begin to increase, and they would transmit themselves to the air in the armlet so that there the fluctuations of volume would likewise increase at that moment (v. RECKLINGHAUSEN, ERLANGER, WYBAUW).

We shall revert to this afterwards, but we must now already call attention to the fact, that on this point the views are still divergent, and that we are still in uncertainty at which pulsations the *mBp* in the armlet is in reality reached.

Moreover the intensity of the pulsations usually increases and decreases so imperceptibly, that it is extremely difficult exactly to draw the line between large and largest pulsations, and consequently too great a margin remains for the subjectivity of the investigator.

The divergency of views with regard to the *MBp.* is still greater.

Soon it appeared that the pulsations in the armlet never ceased entirely, not even if the pressure in it was made very strong. Most likely this may be attributed to the fact that the artery palpitates proximally against the armlet. One tried now to neglect these smallest pulsations, and placed the moment of the *MBp* there, where the pulsations began to decrease. But very often also this moment cannot be exactly determined.

These considerations suggested to WYBAUW, on the track of OLIVER, the idea of constructing a double armlet, the proximal band of which was to receive those so-called "Rand-Pulsationen" whilst a separate distal-band, was connected in a peculiar way with a writing-apparatus (ERLANGER) and noted the fluctuations of volume of the artery. WYBAUW however placed the two bands close to each other. And now it appeared to us that even with a pressure in the two bands greater than the *MBp* the "Rand-Pulsationen" were still transmitted by the upper band to the lower one (compare the curves).

With the present pretty well general use of the broad armlet (only SAHLI still uses the narrow one) another difficulty presents itself.

Let us first consider the *MBp*.

If in the broad armlet a pressure is made, that is a little less than the *MBp*, then the armlet will already be able to close the artery, for just because the armlet is so broad, part of the pressure of the artery will be spent under the armlet. Consequently the pressure in the artery at the lower edge of the armlet will become less than that at the upper edge, whilst the latter is equal to the *MBp*. The pulsations transmitted to the armlet will thus become smaller, before the *MBp* is reached in it. With SAHLI we are of opinion that this is an objection to the broad armlet. It will be the question if the advantage with regard to the surrounding tissues, that the broad armlet undubitably affords (v. RECKLINHHAUSEN), compensates this disadvantage. At all events it would be desirable, that it was generally agreed always to use an armlet of a definite breadth in order to obtain figures that can be compared.

It will at all events have become evident that for the determination of both the *MBp* and the *mBp*, according to this method, much is left to the subjectivity of the investigator. It appeared to us during the observations, made with WYBAUW's apparatus, that, on account of the imperceptible increase or decrease of the pulsations, it is extremely difficult exactly to read the two moments.

B. Palpatory Method.

If one causes the pressure gradually to increase, two moments can be observed at the palpation of the distal pulse. In the first place a moment at which that pulse becomes less intense and secondly a moment at which it disappears. At the first moment the *mBp*, at the second the *MBp* would be reached in the armlet.

For if the pressure of the armlet > the diastolic pressure in the artery, the artery will be closed for a moment during the diastole of the heart. Then a certain force will be required to press the artery open: part of the systolic pulse-wave is consequently checked, distal the pulse becomes less intense.

If further the pressure of the armlet $>$ the systolic pressure in the artery, then even during the systole of the heart the artery remains closed, and consequently the whole pulse-wave is checked: distal no pulse can be felt any longer.

The objections made above against the broad armlet prevail here likewise. As however the surrounding tissues of different persons are likely to be more variable than the part of the pulse-wave that is spent under the armlet, it is perhaps better to continue using the broad armlet. Yet, exactly under a broad armlet, the possibility exists that before the *MBp* is reached in it, the pulse-wave, as a wave, is annihilated, and the blood continues to ooze (PACHON), which, however, cannot be observed at the distal pulse by palpation. (Société de biologie, June 1909).

However, objections exist, both against the determinations with the broad armlet and against those with the narrow one, which do not result from the method of compression but from the palpation of the distal pulse. If it is already often difficult exactly to observe the moment of the disappearance (or the return) of the pulse, the observation of the exact moment of the decrease of the pulse offers very great difficulties. Consequently this method as well leaves too great a margin for the subjectivity of the investigator.

Therefore SAHLI tried to register the two moments. For this purpose he placed a sphygmograph on the distal pulse. Consequently sphygmographically the decrease and the disappearance of the pulsations was recorded. When applying this method SAHLI experienced some difficulties, which were chiefly caused by the veinous congestion occurring in the distal arm at the circular compression; he tried to avoid this difficulty by firmly fastening the sphygmograph. Yet every one who is accustomed to the use of the sphygmograph, and SAHLI himself in the first place, knows how much caution is required when making conclusions from the intensity of the pulsation recorded sphygmographically. A slight displacement of the sphygmograph, a slight increase of the pressure on the spring by swelling of the arm (veinous congestion) and so many trifles more can entirely change the form and the intensity of the sphygmographic pulse.

Therefore this — though an objective — method does not seem to us to be an improvement with regard to the purely palpatory method.

About the so-called *sensatorial method*, by which the patient himself indicates when he feels that the pulsations in his artery begin and cease (beginning and end of the great oscillations) we need not say much. It is only to be applied to intelligent patients, and introduces the subjectivity of the patient instead of that of the investigator, which is at least as bad, and causes by exertion of the attention an increase of the blood-pressure.

The *auscultatory method* (KOROTKOW) by which, distal from the armlet, an artery-tone is heard to become louder or softer in accordance with the different pressures prevailing in the armlet, so that in this way indications must be obtained for the determination of the MBp and the mBp is of course connected with the same drawback of subjectivity.

The same objections hold for EHRET's *method*, who feels the maximal oscillations and the disappearance of the pulse at the artery immediately below the lower edge of the armlet.

None of these methods could therefore satisfy VON RECKLINGHAUSEN, and he tried to find another.

He fills the armlet with water and graphically registers the fluctuations in it by a HÜRTHLE tonograph. On theoretic grounds he admits that if the pressure in the armlet = the pressure in the artery, the arterial wall moves freely, and the amplitude of the pulse-wave is correctly recorded by the tonograph. And at the same time he admits that, as at that moment the pressure in the armlet = the pressure in the artery, the height of the pulse-wave is consequently correctly recorded. Then he divides the pulse-curve into different parts and admits that where a definite part is recorded as greatest, its height is also correctly recorded. From a "Treppencurve" obtained in this way, he construes then an absolute sphygmogram.

SAHLI has given a sharp criticism of this long-winded method, which can be read in the D. Arch. f. Klin. Med. Bd. LXXX 1904, p. 493, and which we are not going to repeat in extenso. He proves that the friction during the passage of the pulse-wave under the — broad — armlet and other factors are as many sources of errors.

In his last publication VON RECKLINGHAUSEN maintains his method, especially because it gives the same figures for the pressure of the blood as the other methods (Beihefte zur Med. Klinik, Hft. 8, 1910). He forgets, however, that just those other methods are not sufficiently reliable on account of their subjectivity.

However it may be, great discrepancy still prevails with regard to the problem of determining the pressure of the blood in man. All methods give us a somewhat unsatisfactory feeling. Moreover VON RECKLINGHAUSEN's method is complicated, his apparatus is expensive and his reading of the curves not in every respect without objection.

It seems that with all methods, even with von Recklinghausen's arbitrariness of the investigator is by no means excluded.

It was on purpose that hitherto we did not mention another difficulty i.e. the factor of the arterial wall.

Usually this factor is entirely left out of account, because it is supposed to be = 0. This opinion is chiefly founded on investigations made on postmortem arterial walls. Yet in drawing conclusions from these investigations one should be very careful. It seems that a short time after death the contraction of the arterial wall and at the same time its rigidity considerably increase. Investigations made at that period have no value for our object.

On the contrary it seems that the arterial wall is very soft and compressible immediately after death, but who will decide if these are not already symptoms of mortification?

And even — who shall decide, if not also in the arterial wall of the living animal, whose artery was laid bare, the contraction and consequently the compressibility has not changed on account of the operation?

And if the arterial wall may not be neglected, the determinations of the pressure of the blood, as they have hitherto been performed, become still less reliable. Is then at the determination of the blood pressure according to the method of the greatest oscillations, this arterial wall included in the determined blood-pressure, or not? Or is perhaps the factor of the arterial wall the cause of the different views that are current about the question: which of the great oscillations are registered at the very moment when the mBp prevails in the armlet?

With the determinations of the blood-pressure, at all events of the maximal one, according to the palpatory method, the arterial wall is almost certainly included.

Could perhaps the comparison of the two methods give us some information about the arterial wall? In our opinion the subjectivity of the methods is too great.

After all that has been said, we cannot be surprised that there is such a great disagreement among investigators concerning the valuation of the influence of the arterial wall. So Leonard Hill found the carotid of a child collapsed by a pressure of 2 $mMHg$; Herringham and Womack found in their determinations of the compressibility of different arteries, 4—18 $mMHg$, in two cases even 30—34 $mMHg$.

Let us for a moment suppose that the factor of the arterial wall is greater than 0, then we can easily understand, why the beginning of the great oscillations, and the greatest oscillations do not occur at the same pressure of the armlet. VON RECKLINGHAUSEN explains this by admitting purely theoretically, that the artery is not compressed long enough to be perfectly closed, if the pressure in the armlet is just a little more than the diastolic pressure; and that the following systolic pulse-wave comes already before the artery is perfectly closed. Consequently only at a higher pressure in the armlet the oscillations will obtain the maximal amplitude.

It may however be asserted that if in the armlet a pressure prevails somewhat higher than diastolic pressure, the artery is only slightly pressed down on account of the resistance offered by the arterial wall, and that not until the pressure in the armlet has increased with the amount required to overcome that resistance, the artery is entirely pressed down during the diastole of the heart, and of course the oscillations have not reached the maximal amplitude before that moment.

From this consideration it might follow that the difference of the two pressures corresponding to the greatest oscillations and the beginning of the great oscillations represents the resistance of the arterial wall.

It may easily be granted that this is likewise a purely theoretical reasoning: yet it explains the gradual increase of the amplitude of the oscillations at an increase of the pressure in the armlet in a more plausible way than the reasoning of VON RECKLINGHAUSEN.

Judging from the objection brought forward above there was great need of discovering a method which, besides enabling to make a reliable determination of MBp and mBp, permitted a valuation of the influence that the resistance of the arterial wall had on these determinations.

Moreover it seemed desirable to make the method as objective as possible, free from all subjectivity both of the investigator and of the patient. And as graphical methods as a rule satisfy this condition of objectivity best, it was evident that, at least for projecting and elaborating the method, graphical registration should be used.

After many researches we have at last come to the conclusion that we might publish the following method, expecting that by careful investigation, also by others, it will prove to answer the requirements mentioned above.

II. DESCRIPTION OF THE METHOD.

After all this method is very simple. *It consists in neither observing palpatory, nor recording sphygmographically, nor overhearing stethos-*

copally, what occurs distal from the compressing armlet, but in registering it plethysmographically.

We take a sufficiently large   comprising the whole forearm and the hand of the patient — firmly closed, not leaky plethysmograph. A simple tin plethysmograph after the model of Mosso is perfectly satisfactory for our purpose. The band of this plethysmograph must be made of thick not over-elastic rubber, and wide enough to surround a normal upper-arm with a slight tension. Care should be taken that the band is long enough to cover the upper-arm to the extent of e. g. 10 cm. In the front part of the plethysmograph the tube is soldered that the rubber tube conducting to the Marey-tambour fits; the membrane-displacements of this little tambour are registered in the usual way on a revolving drum. The whole plethysmographical apparatus is filled with air.

If the plethysmograph is applied in this way, the fluctuations of volume of the arm, which are caused by pulsation and by respiration are recorded on the revolving drum covered by smoked paper. We must directly call the attention to the fact that all motions must of course be avoided by the patient, as these are also immediately followed by fluctuations of volume of the enclosed arm.

Psychical influences do not at all or hardly disturb our investigations, as will appear afterwards.

Now the armlet that is to compress the arm circularly is applied round the rubber band[1]) of the plethysmograph. This armlet is placed in such a way that it surrounds only that part of the plethysmograph-band that closely encircles the upper-arm, so that the lower edge of the armlet lies at some distance above the part of the plethysmograph-band which bends from the arm to the border of the plethysmograph. In order to be sure of this it is advisable to encircle the arm between the border of the plethysmograph and the armlet slightly with a rubber tube (part of a stomach-sound e.g.) that is fastened in that situation. This has likewise the advantage that the part of the plethysmograph-band that has been left uncovered between the tin plethysmograph and the compression-armlet is tightly strained and by turning aside cannot make the curve miscarry. Fixation of the plethysmograph can often prove useful.

For a compression-armlet we used the armlet with two chambers of Wybauw, connected with a mercury-manometer. The proximal chamber of that armlet must receive the so-called "Rand-Pulsationen"

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[1]) In order to avoid misunderstandings, we shall always call the rubber band of the plethysmograph: band, the hollow compression-armlet always: armlet.

whilst only the distal chamber is connected with the registering-apparatus (according to ERLANGER's principle) and registers the pulsations of the encircled artery. With our method we have consequently, at the same time, registered the curve that depends on the principle of the greatest oscillations. Occasionally we have used the narrow compression-armlet of RIVA-ROCCI and then we have not registered the oscillations.

We wrote consequently above each other: 1 the curve according to the oscillatory method, 2 the curve of the plethysmograph. Only the pressure prevailing every time in the armlet was read on the manometer and always immediately registered in the curve.

In order to obtain fine curves, it is advisable to make the patient hold his breath for a few seconds every time when, at a definite pressure, both curves are registered. Otherwise the respiration can always be more or less distinctly observed in the plethysmographic curve, which, though not rendering the reading impossible, causes at all events some difficulty. It is interesting, that even during a pressure in the compression-armlet far above the MBp when certainly all the veins and arteries are tightly compressed, the respiration remains always distinctly visible in the curve. Even then every inspiration lowers the curve a little, every exspiration raises it, and this is the case just as well when compression-armlet and plethysmograph-band are both applied round the upper-arm, as when the former is applied round the upper-arm and the latter round the forearm, and consequently the influence of the one on the other is entirely excluded. This influence of respiration is even to be observed, if the patient's whole arm is tightly held by an assistant. We hope we shall be able to give an explanation of this phenomenon in a subsequent investigation.

At present the communication suffices that in case we wish to obtain fine curves, the patient has to hold his breath each time. However, the moments, that interest us, can for the rest likewise be read with great accuracy with ordinary calm respiration.

How strongly the plethysmograph-band and the compression armlet encircle the arm is of little consequence, if only one takes care to remain below the mBp. This is of course easy to do, and is moreover quite usual. We did not observe a single exception in this respect, not even with very thick arms. And if in the beginning we remain below that pressure, the gradually more and more inflated compression-armlet will exceed the pressure of the plethysmograph-band; consequently this is no longer of any account. There is, however, no objection to taking a wide band, which does not even press a thick arm, as the compression-armlet will bring about the stopping up of the plethysmographic apparatus towards the upper-arm.

After this introduction we may proceed to the *experiment*:

For this purpose we quickly increase the pressure in the compression-armlet, till it certainly surpasses the *MBp*. This must be done quickly in order to prevent the veins of the arm from filling abundantly. At a slow augmentation of the pressure in the armlet this would occur, as the veins are certainly sooner obliterated than the arteries. Therefore we must proceed rather quickly. Then the arteries shut themselves soon after the veins. Some veinous congestion certainly occurs but this is no impediment. If the pressure in the armlet has reached a height that doubtlessly exceeds the *MBp* in the artery, then we let simply the surplus pressure, occasioned by the veinous dilation of the arm, escape through a valve in the tube of the plethysmographic apparatus, and consequently the curve begins, whilst in the plethysmograph atmospheric pressure prevails. Then the valve is carefully closed.

The further course of the experiment can best be demonstrated by following the curves. All curves have a typical form and are very easily registered. After some practice failures need not occur.

Let us take as an instance the curve obtained from J. P. V. (a normal individual, 26 years 17. I. 1911 Fig. I).

We began with a pressure in the armlet of Wybauw of 160 mm. Hg. and made the drum revolve a few seconds. Neither in the plethysmographic curve, nor in the curve of the armlet itself any pulsation is seen. Consequently a pressure was reached that certainly surpassed the *MBp*. After having stopped the drum, we lowered the pressure to 150 mm. Hg. If we made the drum then revolve again for a few seconds we did not see any pulsations either.

In this way we constantly lowered the pressure a few mm. Hg. and registered the curves.

At 145 mm. Hg a feeble pulsation is observed in the curve of Wybauw's armlet, in the plethysmographic curve we do not yet discover anything. We see the same at 140 mm. Hg. Now one must remark that the plethysmographic curves at 160, 150, 145 and 140 mm. Hg are registered nearly all at the same level on the drum.

A great change however takes place at 135 mm. Hg. Suddenly the plethysmographic curve goes upward. *This means consequently that blood penetrates into the arm.* For ascension of the curve means that the membrane of the Marey-tambour is lifted up. This means increase of the pressure of the air in the plethysmographic apparatus, and this must be the consequence of swelling of the arm. And the only cause why the arms swells can be that under the WYBAUW armlet blood penetrates into the arm. As a proof for the accuracy of this reasoning must be admitted the plethysmographic curve registered at this pressure, in which a slight pulsation — for the first time — can be observed.

Here we have doubtless before us: *the moment of the MBp*. That is to say that in that *MBp* of course the factor of the arterial wall is included. For the latter will be of use to open the artery.

At this moment the oscillatory curve shows nothing particular that could not be observed at a former pressure.

Now we wait quietly till the lever of the MAREY-tambour does not rise any longer. This takes some time. If at last the lever rises no more, we see as a rule that it continues in the position it has reached. We shall afterwards revert to exceptions. In case of doubt we register a second, third etc. curve at the same pressure. If then really the lever remains at the same height, we know of course that the arm does not increase any more in volume, and consequently the slight pulse-wave that passes under the compression-armlet is no longer able to increase the volume of the arm.

Then we lower the pressure with e. g. 5 mm. Hg. (in our case to 130 mm.).

The curve again moves upward and the pulsation becomes more distinct. Both occurrences are proofs that the artery opens more widely. No change is to be seen as yet in the oscillatory curve. Again we wait calmly till the end of the upward move, register eventually another curve (comp. the example).

Now we lower the pressure to 127 mm. Hg and after a few moments we see the plethysmographic curve go down rather rapidly. What has happened?

During the pressures of 135 and 130 mm. Hg blood continued to flow into the arm because the arteries were open and the veins still closed. This blood flowed through the arteries, through the capillaries towards the veins, and would have left the arm again, if in the veins it had not been arrested by the compression-armlet and kept back there. Consequently the volume of blood in the arm increased, and the plethysmographic curve rose, and continued to rise of course till the pressures distal and proximal of WYBAUW's armlet are equally balanced.

Now we may consider the arteries + capillaries + veins as a system of communicating vessels, and certainly so, if we work slowly. As long as the pressure in the veins is lower than that in the arteries, blood will flow from the arteries into the veins, and consequently the volume of the arm will increase as long as the veins are still tightly compressed. This will continue till the pressure in the veins has become equal to that in the arteries. Consequently, if only we work slowly enough, the arterial blood-pressure will at last prevail in the veins, i.e. the pressure of the blood-column itself, whilst the influence of the arterial wall is of course excluded.

Not before this pressure in the veins, which must consequently be inferior to arterial pressure + arterial wall, and is supported both by the parietes of the veins and the surrounding tissues, surpasses the pressure in the compression-armlet, the blood under that armlet will be able to flow again from the veins to the heart. But at that moment the volume of the arm will decrease again, for the fall in the veins distal and proximal to the armlet is at that moment enormous.

Now the volume of the arm diminishes in our case at a pressure of 127 *mm.Hg.* The downward move of the registered curve proves it likewise.

As we may neglect the parietes of the veins as factor, *this pressure is consequently the real pressure of the blood without the factor of the arterial wall.*

A fortiori we may regard the arteries + capillaries + veins as a system of communicating vessels, if we take into account LEONARD HILL's words: "that there are wider channels connecting the arteries and veins through which the pressure is transmitted to the veins. The existence of such wide channels is recognised by histologists." (Further advances in physiology, 1909, p. 143).

In the beginning we simply waited till the lever of the MAREY-tambour did not move upward any longer. Then we diminished the pressure. In this way we obtained as factor for the arterial wall with normal persons about 15 mm.Hg. (40 observations).

Then LEONARD HILL and MARTIN FLACK's article in the Journal of Physiology vol. XXXVIII came to our hand. In order to determine the exactitude of the palpatory method they proceed from the same idea as we, viz. that in the end the same pressure prevails in the veins as in the arteries, if the latter are open, and the former tightly compressed. Their experiment is best cited in their own words:

"We place one armlet round the brachial artery, and another narrower one round the forearm of the same arm — each connected with a manometer. We find the obliteration pressure with the first armlet. Suppose it is 150 mm. Hg. We lower the pressure in this armlet to say 145 mm. Hg. so that arterial blood can get through into the limb, but cannot get out of the veins of the limb until the pressure in the veins rises above 145 mm. Hg. Allowing time for the veins to fill, we then measure the pressure in one of the superficial veins and find that it does finally reach this pressure We raise the pressure in the second armlet, observe the pressure at the moment when the vein fills from below. One of us watches the vein and signals the moment of filling, the other reads the manometer. We repeat the observation several times. If we find the pressure in the vein reaches 145 mm. Hg, we know that the obliteration pressure was correct within 5 mm. Hg. To carry out this method a vein must be chosen which does not fill from above or at any rate quickly. With such high pressures in the veins the valves leak, and this makes quick working necessary. In cases of high pressure it is necessary to give a rest between each test as the maintenance of the first armlet at a pressure close to the obliteration pressure is rather painful.

From the above observations we conclude that the obliteration method of measuring the arterial pressure is correct within 5 mm. Hg, even in cases where the arterial wall is markedly changed from pathological causes.

One sees what startling similarity there is between this method and ours, with regard to the point of issue. And at the same time one sees that LEONARD HILL and MARTIN FLACK's experiment has proved that — when working in this manner — one may consider arteries + capillaries + veins as a system of communicating vessels.

Though HILL's determination of the "obliteration pressure" is made after the palpatory method and consequently has the incorrectnesses of subjectivity, described in our first chapter; and though, as one can read in the description, the determination of the pressure in the veins is connected with some difficulties, yet there was in this publication an incitation for us to make a new series of experiments, in which we proceeded still slower. Though we shall afterwards revert to the general conclusions, yet we can now already state that in the beginning the factor of the arterial wall was most likely valued too high by us, but at the same time that the arterial wall may not entirely be neglected.

To return to our case we may thus give as figures there:

$MBp + Aw$ between 140 and 135 = 137 mm. Hg.
MBp between 130 and 127 = 128 mm. Hg.
Consequently: Aw = 9 mm. Hg.

That the fall of the plethysmographic curve is in reality caused by the veinous blood being pressed from below the compression-armlet to the heart appears from a peculiar behaviour of the oscillatory curve, as it can often be seen and controlled at the manometer. If we look at curve II (D. M., normal individual, 31 years, 6 I 1911) we see the oscillatory curve rise at 107 mm. Hg. This is occasioned by the veins beginning to press the blood under the compression-armlet, so that the pressure in it increases, for the volume of the arm at the place of compression augments. We see consequently the mercury in the manometer rise a few mm. And if now we lower the pressure in the armlet, the passage under it is forced by the veinous blood, and the oscillatory curve goes down again (in our case at 106 mm. Hg).

It is clear that, if Pachon is right, namely that under the broad compression-armlet the pulse-wave can be annihilated at a certain pressure, and yet the blood continue to ooze under the armlet, (comp. p. 1184) that in that case the palpatory method for dertermining the $MBp + Aw$ fails; our method however does not, as the oozing of the blood will likewise swell the arm and consequently make the plethysmographic curve rise.

After these elucidations it appears to us that our method enables us to determine the $MBp + Aw$ exactly and to estimate the factor of the Aw.

One remark must still be made. We found like Hill and Flack that at high bloodpressure — but only then — the slow operation could become painful for the patient. And as it is admitted that pain can raise the bloodpressure it might be possible that our determination of the Aw consequently became incorrect (too small). This objection also holds for Hill and Flack's experiments. In such cases it is therefore necessary to raise the pressure again quickly to just a little above the $MBp + Aw$ that has been determined before, and to see if the pulsation has disappeared. If not, then it is necessary to determine the pressure at which the plethysmographic pulse disappears again. This method however gives less beautiful results. It seems that occasionally at very high Bp, the Bp rises a few mm. during the slow phase of the experiment. At lower Bp the pain is not felt.

After having noted a few times more the curve at lower pressure (120, 115, 110 mm.) in order to state that now really, when lowering the pressure, a gradual fall takes place, we open, in order to determine the mBp, the valve of the plethysmographic apparatus for a short moment, and let the surplus pressure escape from it. We repeat this at every further diminution of pressure in order to have in this way the following curves registered at the same level. This is necessary for the following reason.

We had hoped that at the moment of the mBp something similar would occur in the arteries and veins to what is observed at the moment of the MBp. Sometimes we suppose that from the rise and fall of the curve we can read something about the mBp and the Aw, but it appeared that this was not regularly the case. We made several experiments, but continued to be unsuccessful. Therefore we have been obliged to desist from determining the mBp and the $mBp + Aw$ in this way. We only succeeded — by another method — to determine the $mBp + Aw$ from the plethysmographic curve. From what we know already about the Aw, we can, however, easily calculate the mBp alone.

In order to determine the $mBp + Aw$ we act as follows:

After having closed the valve again we recorded once more the curve at 110 mm. Hg. Then every time the pressure was lowered 5 mm. Hg, the valve of the plethysmograph was opened, shut again and the curve recorded.

After fixation of the whole curve, the amplitude of the pulsation was measured at every observed pressure. Now it appeared that this amplitude gradually increased till, beginning from a definite pressure, it became constant, and only decreased again a little at very low pressure (because the armlet at that pressure fitted less tightly round the arm).

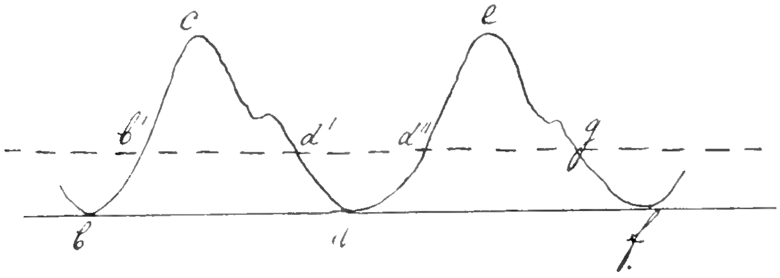
We need not say that, as we were now trying to gather information from the amplitude of the pulse-wave, it should be registered everywhere at the same level.

In our opinion consequently the pressure at which, operating in this way, we saw the pulsation show for the first time the maximal amplitude, is the $mBp + Aw$.

To understand this we had best reverse our reasoning — as if from 0 we constantly raised the pressure.

Thereby we must keep in view that the pulse-curve of the plethysmograph is a volume-curve.

If now the pressure in the compression-armlet is lower than the



mBp, then at each heart-systole the whole volume of blood will still pass under it, and the plethysmograph-curve shows us the changes of volume that result from it.

This will also take place when the mBp ($+ Aw$) has just been reached.

When, however, the pressure becomes a little higher than that $mBp + Aw$, then the artery remains shut during part of the pulsation.

Instead of the entire volume bcd only $b'cd'$ passes under the armlet during each heart-systole. A part is constantly arrested by the pressure, the volume of blood passing under the armlet becomes smaller and from that moment the volume-curve of the plethysmograph consequently becomes smaller. This moment lies thus a little above the $mBp + Aw$, and the moment before was the $mBp + Aw$.

Sometimes it can at the same time distinctly be seen that, if the pressure reaches just a little above the $mBp + Aw$, not only the pulse-wave of the plethysmograph becomes smaller, but that also a diastolic pause can be observed in it. For during the time $d'—d''$ no blood is thrown into the arm. Very often, at all events the latter part of the pulse-wave has become much more horizontal. This occurrence consequently, when it presents itself, furnishes a good control for the diminution of the pulsation.

In our curve I the diastolic pause is not visible but the diminution of the pulse at 80 mm. Hg can be distinctly observed. In curve III on the contrary the diastolic pause at 85 and especially at 90 mm. Hg can be very well distinguished

In our example curve I is consequently:

$$
\begin{aligned}
mBp + Aw \quad &= 75 \text{ mm. Hg} \\
Aw \text{ (comp. above) was} \quad & \ 9 \text{ mm. Hg} \\
\text{Thus } mBp &= 66 \text{ mm. Hg.}
\end{aligned}
$$

The phenomena regarding the amplitude of the plethysmographic pulse occur, whether the manometer is connected with the armlet or whether it is pinched off, and consequently do not depend upon the mercury-fluctuations. With the simultaneous registration of the two curves it is, however, peculiar, that the last great pulse-waves of the plethysmograph and the greatest oscillations usually show themselves at the same pressure, which agrees entirely with our views concerning the signification of the greatest oscillations (comp. Chapter I).

If we closely examine the oscillatory curve, we see how difficult it is to find out with certainty the beginning of the oscillations that are to indicate the MBp. And we see at the same time, how it is almost impossible to determine beginning and end of the great oscillations. And according to our experience this is often the case. We have already said that the oscillation-curves do not teach us anything about the *Aw*.

Before continuing we must call the attention to the fact that one should take care not to be deceived by the expansion of the air in the plethysmograph by warmth. Whoever is conversant with the method sees immediately, what is the consequence of the air in the plethysmograph becoming gradually warm, and what must be attributed to the pulse-wave entering into the arm. Moreover one can easily introduce into the plethysmograph air that has been previously warmed, or wait till the air in it has obtained a constant degree of warmth. The latter method takes time, but this is rather an advantage than a disadvantage. Every first determination of the *Bp* whatever instrument may be used, gives, on account of psychical influences, too high figures, and only the subsequent determinations, when the patient is no longer afraid of the instrument give constant figures. Consequently there is no objection to making a first determination whilst the air is becoming warm, by which the patient overcomes his fear of the instrument and the operator gets orientated.

It is with *Bp*-apparatuses as with thermometers. The so-called thermometers "à la minute" must just as well lie 10 minutes in the axilla as the ordinary ones, because the axilla has not assumed the warmth of the body before that time. So neither quick determinations of the *Bp* can be made, because the patient must first overcome his fear of the instrument. If once the patient is familiar with the instrument then, the next day or a following time, the first determination is more reliable.

III. RESULTS OBTAINED.

Up till now we made on various persons 172 determinations in all, 40 of these were taken at nephritis, 4 at insufficientia aortae, 3 at arterio-sclerosis, 1 at the disease of STOKES—ADAM, and the rest at tub. pulm., anaemia, arthritis, nervosism and normal individuals. It is impossible and unnecessary to give all these figures here. We shall only select a few at random.

So of our example the figures were:

1. *J. P. V.* 27 years (norm.)	MBp + Aw.	155	140	137	137
	MBp	145	129	128	125
	Aw.	10	11	9	12
	mBp + Aw.	75	75	75	75

The third row of figures belongs then to curve I.

From the patient, from whom curve II was obtained, a few more complete curves were taken.

2. *D. M.* 31 years (norm).	MBp + Aw.	115	112
	MBp	106	106
	Aw.	9	6
	mBp + Aw.	80	80

From the patient of curve III (5th row):

3. *H. v. L.* 27 years. (norm.)	MBp + Aw.	115	125	120	115	119
	MBp	108	117	110	108	113
	Aw.	7	8	10	7	6
	mBp + Aw.	75	70	75	75	80

From the female patient of curve IV (3rd row):

4. *M*^{rs}. *Sch.* 70 years (art.scler.).	MBp + Aw.	154	147	145
	MBp	—	138	140
	Aw.	—	9	5
	mBp + Aw.	100	95	90

And finally from the patient of curve V (3rd row):

5. *J. v. N.* 24 years (neph. chr.)	MBp + Aw.	147	148	152
	MBp	137	139	137
	Aw.	10	9	15
	mBp + Aw.	110	110	100

We found the following averages (with Wybauw's armlet):

A. *Normal*	15—20 years	21—40 years	41—60 years	over 60 years
MBp + Aw.	114	121	132	145
MBp	104	112	125	139
Aw.	10	9	7	6
mBp + Aw.	70	75	76	86
Pulse amplitude	44	46	56	59

B. *Nephritis chron.*	
MBp + Aw.	162
MBp	149
Aw.	13
mBp + Aw.	104
Pulse amplitude	58

C. *Insufficientia Aortae* (Riva-Rocci's armlet).	
MBp + Aw.	157
MBp	140
Aw.	17
mBp + Aw.	70
Pulse amplitude	87

D. *Disease of Stokes-Adam* (WYBAUW's armlet).

MBp + Aw.	197
mBp + Aw.	80
Pulse amplitude	117

A few determinations of the arterial wall were too great because the determination was made too quickly. Not taking into account however these determinations we were struck by the fact, that the factor found for the arterial wall with the same person, is rather constant, even with different *MBp*. This proves of course strongly in favour of the method.

Only once in the 172 determinations the determination of the *MBp* + *Aw* is doubtful, most likely on account of the influence of the expansion of the air in the plethysmograph by warmth. All other determinations could be read with perfect accuracy.

The determination of the *MBp* without the *Aw* requires greater care and to state this we may not be satisfied with a few determinations.

With normal persons as a rule the *MBp* increases with their ages and so does the *mBp*, which was not unknown.

The *Aw* factor does not vary in the same degree. On an average it is 6—10 mm. Hg. Consequently the mistake is not great, if we consider for normal people the *MBp* + *Aw* determined according to the obliteration-method as the maximal blood-pressure. And with our method the latter can be quickly and easily determined, whilst the determination of the *Aw* requires time, and is somewhat painful with high blood-pressure. But it is only so with high blood-pressure. One of our patients with a maximal blood-pressure of 135 mm. Hg. did not feel any pain, another with a maximal blood-pressure of 170 mm. Hg. did feel pain.

In general the figures found by us do not deviate from those which are usually admitted as normal.

It is remarkable that the influence of the *Aw* that was found with arteriosclerosis was very slight. Perhaps we may not conclude too much from our single case. Yet a slight influence of the *Aw* with strongly pronounced arteriosclerosis would perhaps not be fully inexplicable. In such an arterial wall we find besides calcified parts which undoubtedly offer a greater resistance to the compression than a normal wall, certainly also degenerated parts of the nature of a fibrous tissue, the elasticity and resistance of which have diminished. This view seems to be confirmed by the decrease — though only in a slight degree — of the *Aw* with the age.

The influence of the *Ar* is often stronger than normal, for the observations we made, with chronic nephritis. Nor need this fact remain unexplained, for we may admit that a contracted artery hard pulse of the nephritici — will offer a greater resistance to the compression than a normal artery.

It is remarkable that after these observations we found a report of an article of JANEWAY (Lancet March 1911) in which this investigator also comes to the conclusion that with arteriosclerosis the arterial wall has little influence on the determination of the blood-pressure, a contracted arterial wall on the contrary has great influence!

To be short, we are convinced that our method procures reliable information about *MBp* and *mBp*, and gives an impression of the factor of the *Ar*.

In order to determine averages of the *Bp* with normal men of different ages and with various diseases still more determinations must be made.

The same is necessary if we wish to compare the results obtained with the narrow and the broad compression-armlet. Though it seems to us that higher figures are obtained with the narrow armlet, we have not yet made a sufficient number of comparative determinations to express a decided opinion on this head.

Microbiology. — "*Lipase produced by Microbes.*" By N. L. SÖHNGEN. (Communicated by Prof. M. W. BEIJERINCK.)

(Communicated in the meeting of March 25, 1911).

In a previous paper[1]) a number of fat-splitting bacteria were described which occur very generally in nature; at the same time the way was indicated by which these species may be distinguished from others and how they are brought into pure culture from the soil, sewage water, milk, or rancid butter.

Among the yeasts and moulds, too, we meet many species that form lipase. Thus most yeasts contain endo-lipase; at abundant nutrition they are able to store up fat in the cell, and can use it again when less favorable culture conditions occur.

Only a small number of yeast species secrete diffusing lipase; to these belong some species often found in milk, among which a *Torula*. Fat-splitting yeasts may be obtained from garden soil by inoculation into a medium of the composition: 100 tap-water, 1 fat,

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[1]) These Proceedings XIII, p. 667.

0,05 KCl, 0,05 NH_4Cl, and 2 to 4 drops of phosphoric acid, with aërobic cultivation at 20°—25° C. The isolation of the fat-splitting yeasts is then effected by sowing the culture in which they are accumulated on yeast-glucose-gelatin with calcium carbonate, solidified in a culture box on a thin layer of fat. The colonies of the fat-splitting yeasts are signalised on this medium by their hydrolising the fat.

Diffusing lipase is much more commonly secreted by moulds than by yeasts. Fat-splitting moulds can be best isolated from rancid fats. From the air, also, fat-splitting yeasts and moulds are obtained by exposing the said medium for some time to the air and subsequently isolating those organisms which have splitted fat under the colony.

Fat-splitting bacteria, yeasts, and moulds, all secrete a lipase possessing the same properties as shown by many experiments.

Consequently, although the following researches are for the greater part carried out with lipase formed by bacteria, the thereby obtained results hold true as well for the lipase of yeasts and moulds.

Formation of lipase by microbes in culture media of different composition.

When fat-splitting microbes are cultivated in media of different composition, it is found that in media wherein they grow, also lipase is formed.

Thus, *B. lipolyticum*, *Oïdium lactis*, *Torula*, *Penicillium glaucum*, secrete lipase when cultivated in tap-water to which is added 0,05 °/₀ bikaliumphosphate, one of the following carbon sources: glycerine, glucose, calciumlactate, or natriummalate, and one of the nitrogen sources: peptone, asparagine, ammoniumchlorid, or kaliumnitrate.

The nature of the carbon and nitrogen sources is thus of no consequence for the formation of lipase by micro-organisms which assimilate them, that is to say, if a carbon or nitrogen source, what, ever be its composition, is assimilated by a fat-splitting organism, it will serve for the production of lipase by that organism.

The composition of the medium, however, exerts its influence on the quantity of secreted lipase.

By a certain number of microbes the greatest quantity of lipase is secreted when the culture conditions are the most favourable. This fact can be demonstrated in a simple way by a method with tubes coated with fat.

Various substances, however, exert a retarding influence on the secretion of lipase by microbes, namely such compounds as sugars and alcohols, from which they form acids.

Influence of acid and alkali on lipase.

The great influence of acids on the decomposition of fat by lipase produced by microbes, is most evident when the microbes which form acid from glucose, such as *Penicillium glaucum, Oïdium lactis, B. lipolyticum α, B. Stutzeri,* or *B. fluorescens liquefaciens,* are cultivated on brothagar with 5 °/₀ glucose, solidified on a thin layer of fat in a culture box, or in a fatted tube of broth with 5 °/₀ glucose. These microbes do not split fat in the medium by diffusing lipase; the fat remains quite unaltered. It is true that it is slightly attacked through direct contact, for example by the mycelium of moulds, when this has grown through the agar and subsequently touches the fat, or by bacteria in the tubes when in a layer near the surface they locally also touch it. The decomposition of the fat does not, however, take place deeper in the tube and it is always excluded when there is some distance between the fat and the organism.

In the accompanying figures *A* and *B* may be observed the influence of acid formation and of the presence of acid in a medium on the action of microbic lipase.

A represents a culture box with broth-gelatin solidified on a layer of fat.

B is similar to *A* but contains broth-gelatin to which 5°/₀ glucose has been added.

On both media streaks are made only of fat-splitting bacteria, in the way as indicated in Fig. 1.

In *A* all the bacteria make fields of splitted fat, as is distinctly to be seen; this is not the case in *B* where *B. Stutzeri* and *B.*

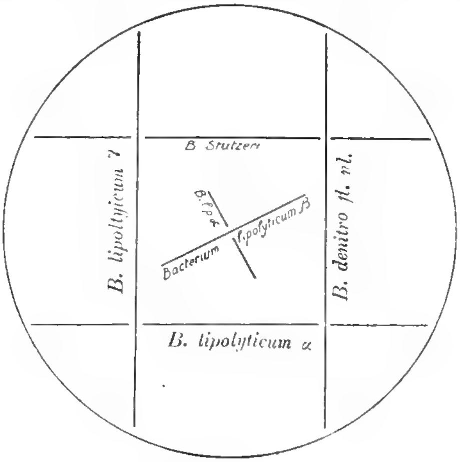

Fig. 1.

lipolyticum α, which form acid from glucose, do not split. We likewise observe that the presence of acid also prevents decomposition of the fat by the lipase produced by the bacteria which do not form acid from glucose; this is distinctly to be seen by the narrowing of the fields at the points where the inoculation streaks cross.

It would, however, be erroneous to draw the conclusion that in cultures where the fat is not decomposed by the formation of acids, lipase is neither secreted. That this enzyme is indeed present is proved by neutralising such a culture after addition of an antisepticum; already after some hours a distinct decomposition of the fat is to be observed; it is not, however, so vigorous as in cultures where no acid formation has taken place, although the microbes in cultures with glucose thrive often better than in those without it. But if calciumcarbonate is added to culture media containing glucose, the acids formed by bacteria are neutralised, the fat is then decomposed nearly as vigorously as in cultures containing no glucose and carbonate. These facts may be stated very simply as well with the help of fatted tubes as by means of plate cultures.

At a certain degree of acidity fat is no more decomposed by the lipase, which was shown by a series of tubes filled with an increasing quantity of acid, in this case lactic acid, with a quantity of a culture of fat splitting microbes. It is found that the decomposition of the fat decreases as the rate of acid rises, and that it ceases entirely when the culture liquid is about $^1/_{50}$ N. acid.

This acid-limit for the action of the lipase is the same for the enzymes of *B. Stutzeri*, *B. lipolyticum α*, *B. lipolyticum B*, and of *Oïdium lactis*.

The lipase is rendered inactive as well by mineral as by organic acids, the former act more vigorously on the ferment than the latter, so that a lipase preparation, inactivated by mineral acids, after neutralisation is considerably less active than the same preparation treated with an equal quantity of an organic acid and subsequently neutralised. It is some time before the splitting power of the lipase is restored; this depends on the nature and the volume of the acid used. Whilst, for example, in a culture containing lipase, after acidification with lactic acid to $^1/_{10}$ N. and subsequent neutralisation, the decomposition of the fat became already visible after one hour's cultivation at 37° in a tube of neutralised culture, this lasted 6 hours when phosphoric acid of the same concentration had been used, the same culture conditions being observed.

Determination of the influence of acid and alkali on fat-splitting by microbic lipase.

The influence of acid and alkali on fat-splitting by this lipase was ascertained as follows.

Ten experiment tubes were filled with 15 c.c. of a neutral thymol-containing culture of lipolytic bacteria, 10 c.c. of a 10°/₀ fat emulsion in agar, and into the tubes from 1 to 10 were introduced respectively from 2 to 24 drops of a concentrated lactic acid solution in water, so that each contained respectively from 1 to 12 c.c. $^1/_{10}$ N acid.

A second series of tubes treated in the same way, contained instead of lactic acid ammonium-carbonate, so that from 1 to 10 they contained respectively 1.8 to 18 c.c. $^1/_{10}$ N ammonium-carbonate. After 8 hours at 37° C. they were quickly cooled to 7° C. and titrated. For the neutralisation of a 10°/₀ fat emulsion in agar 0.45 c.c. $^1/_{10}$ N acid is required.

The results of these experiments are united in the following tables.

Influence on fat-splitting by microbic lipase.

c.c. $^1/_{10}$ N Lactic acid	0	1	2	3	4	5	6	8	10	12
after 8 hours at 37° C.	0.8	1.5	2.3	3.1	4	4.7	5.6	7.5	9.5	11.5
Quantity of lactic acid formed in c.c. $^1/_{10}$ N.	1.25	0.95	0.75	0.55	0.45	0.15	0.05	—	—	—

Fat-splitting by Ammoniumcarbonate.

c.c. $^1/_{10}$ N Amm. carb.	0	1.8	3.6	7.2	10.8	14.4	18.
c.c. $^1/_{10}$ N acid used after 8 hours at 37° C.	0.45	0.55	0.75	1.2	1.4	1.75	2.10
fatty acid formed.	0	0.10	0.30	0.75	0.95	1.30	1.65

Influence of Ammoniumcarbonate on microbic lipase.

c.c. $^1/_{10}$ N acid formed.	1.25	1.55	2.05	2.95	3.15	3.75	3.90
Fatty acid secreted by action of Amm. carb.	0	0.10	0.30	0.75	0.95	1.30	1.65
Fatty acid formed by the action of lipase in c.c. $^1/_{10}$ N.	1.25	1.45	1.75	2.2	2.2	2.45	2.25

These experiments prove that in a medium with a lactic acid concentration of about $^1/_{50}$ N no more fat-splitting by the lipase takes place. The action of the lipase on fat is much favoured by the presence of alkali, in this case ammoniumcarbonate, and it is most effective when the medium titrates about $^1/_{25}$ N alkali.

It is obvious from the above tables that the action of the lipase depends on the concentration of the hydrogen and of the hydroxylions, the former exerting a retarding, the latter an accelerating influence.

From these observations it follows that rancidity of dairy products can only then be caused by lipase when the acid degree of these products is below $^1/_{50}$ N. This will be the case when the lactic acid in butter or cheese, which at first exceeds by far the said concentration, has lowered to $^1/_{50}$ N, through the action of alkali-producing bacteria and moulds; they neutralise and oxidise the present acid, whilst besides, by the formation of calciumcarbonate by the oxidation of calciumlactate, acid is also neutralised.

Influence of various compounds on the fat-splitting by microbic lipase.

It was found of importance to consider in how far other compounds than acids and bases act on fat-splitting by lipase. For these experiments it is desirable to work with a lipase preparation, which, besides the enzyme, contains no or only extremely small quantities of compounds that might act on the splitting-process. Such a preparation is satisfactorily obtained by dialysis of the medium whereon the lipase-microbe has grown or by precipitation of the enzyme from it.

Dialysis of the microbic culture proceeds very slowly, so that it must be continued some weeks, when parchment paper dialysators are used, before the dialisable compounds are sufficiently diluted to make the experiments succeed.

The results obtained with such a lipase preparation are to my opinion not quite trustworthy as during the long time of the dialysis number of processes may go on in the complex culture liquid. By means of greased tubes, however, it could be stated that the fat-splitting power of the culture decreases during the dialysis, the dialysate containing no lipase or only very small quantities. When the dialysate is again added to the dialised culture, the fat-splitting power of the mixture is greater than that of the culture to which as great a volume of water has been added as in the previous case c.c. dialysate; it was also found that slight quantities of calcium and magnesium salts act favourably on the decomposition.

It is possible in a very short time to procure a microbic-lipase preparation, quite answering the said requirements and which enables, moreover, auxanographically to observe the influence of various compounds on fat-splitting, namely by dialysis of a solid medium.

This is effected in the following way:

The surface of a broth-agar plate in a glass box is rubbed with a culture of fat-splitting microbes and allowed to stand about 8 days at ± 25° C. In that time the bacteria have grown and produced lipase which is diffused in the agar. Now the bacteria are washed off the agar with water containing thymol, whereupon the agar is removed from the box and put into a vessel of distilled water. If now during the first 24 hours the water is a few times refreshed, the agar contains only very small quantities of dialisable compounds after 36 hours whilst of the slowly diffusing lipase a sufficient amount for the experiments remains behind.

When this agar is put on a fat-layer in a culture box the fat is only very feebly decomposed over the whole surface; on the other hand, compounds brought on the agar and favouring the decomposition of the fat produce a white field.

In this way it was stated that the following compounds favour very much the decomposition of fat by lipase: calciumsulphate, calciumchlorid, magnesiumchlorid, natriumbicarbonate, ammoniumchlorid, ammoniumsulphate, trimethylamine, natriumglycocholate, particularly calcium- and magnesiumsalts, natrium glycocholate and trimethylamine; whilst kalium, natrium, ferric and manganese salts exert less influence. In general it may be observed that small quantities of electrolytes favour the fat-splitting by lipase. In the same way it was stated that methyl-, aethyl- and amylalcohol retard the process, sugars and glycerine being of no influence.

Analogous results were obtained by experiments with lipase precipitated from a microbic culture by means of alcohol.

From these facts follows that lipase produced by microbes presents a great similarity to liver- and pancreatic lipase.

The investigations of POTTEVIN, KANITZ, HENRI, LOEVENHART and MAGNUS have shown that calcium ions and natrium glycocholate are very favourable to the process of fat-splitting. The fat-splitting power of liver extract diminishes by dialysis whilst substitution of the dialysate to the dialised extract again gives an active lipase. As co-enzyme natrium glycocholate may be substituted instead of the dialysate, with the same result.

By means of pancreatic lipase POTTEVIN succeeded to prepare fat synthetically in a biochemical way; we shall see that also with the help of microbic lipase fat is formed from a fatty acid and glycerine.

Acid-lipases.

From the researches treated in the beginning of this paper about the influence of acids on the action of lipase it might already be concluded, that lipase forms a labile compound with acids, which is easily decomposed by alkalis. The results of the following experiments will show this still more clearly, besides they will expose some properties of these compounds.

The diffusion of acid-lipase and its decomposition by neutralisation we can demonstrate as follows.

The bottom of a glass box is coated with a thin layer of fat and on it are consecutively poured three layers; broth-gelatin with 4°/₀ glucose, broth-gelatin with 4°/₀ glucose and calcium carbonate, and again broth-gelatin with 4°/₀ glucose only.

If now we bring on this medium fat-splitting bacteria which form acid from glucose, acid-lipase, which does not decompose fat, as we have demonstrated, diffuses through the upper layer of broth-gelatin glucose; the acid is subsequently neutralised in the carbonate layer and the lipase diffusing through the second broth-gelatin-glucose layer reaches and splits the fat.

A compound of lipase and higher fatty acids is, in opposition to the above named acid-lipase, insoluble, it does not diffuse through the culture medium.

This can be shown as follows.

On broth-gelatin, solidified on a layer of fat, a thin layer of finely divided fatty acid is placed, in the same way as a layer of calcium-carbonate in the former experiment.

If we cultivate on this culture plate fat-splitting micro-organisms the said lipase diffuses in the gelatin and is fixed in the fatty-acid layer. The layer of fat at the bottom of the box remains unaltered. I have sometimes left such cultures for more than a month at ± 22° without any decomposition being visible, whilst through a gelatin layer of the same thickness as the above, ± 3 mm., a very obvious decomposition of the fat by the diffusing lipase was observed already after 4 days' cultivation.

Thus, although lipase does not diffuse through the layer of fatty acid, it does do so in the form of acid-lipase. Moreover it is possible to convert the lipase from the insoluble fatty-acid compound into a diffusing acid-lipase by means of mineral or organic acids, such as lactic acid and butyric acid.

These two properties of the lipase can be demonstrated by a combination of both the foregoing media. Starting from the bottom the succession is then: a fat layer, gelatin, gelatin and calcium-carbonate gelatin, gelatin and fatty acid, gelatin, the gelatin consisting of broth-gelatin and 5 °/₀ glucose.

On this medium, about 0.5 cm. thick, a fat-splitting microbe is cultivated, which forms acid from glucose, for example *B. lipolyticum α*, and one which does not do so, such as *B. lipolyticum β*. After two weeks' cultivation fat-splitting is to be observed under *B. lipolyticum α*, whilst under *B. lipolyticum β* no splitting is seen. Hence, the acid-lipase under *B. lipolyticum α* diffuses through the fatty-acid layer, is neutralised by the carbonate layer and the further diffusing lipase decomposes the fat. The lipase of *B. lipolyticum β* combines with the fatty acid and diffuses no further.

But if now one of these acids is transported to the place where *B. lipolyticum β* has grown, it diffuses through the gelatin, forms with the lipase which is combined with fatty acid an acid-lipase, which diffuses and is decomposed in the carbonate layer, the further diffusing lipase decomposing the fat. It needs no explanation that lipase is likewise freed when the fatty acid is neutralised by addition of alkalis so that then also fields of decomposed fat arise.

Hence, microbic lipase behaves in all these experiments as a feeble alkali forming compounds with acids and again is freed from these by alkalis.

Influence of oxygen and light on the decomposition of fat by lipase produced by microbes.

Presence of oxygen and light favour the decomposition of fat by the action of lipase.

The favourable influence of oxygen on the decomposition of fat is very simply shown by means of fatted tubes filled with a lipase-containing gelatin. If some tubes are quite filled with the gelatin and some others thinly coated with it as is done at the preparation of roll-cultures, it is found that in the full tubes, where thus no oxygen can enter, the decomposition of fat proceeds much more slowly than in the other tubes; still there is more lipase in the former than in the latter although in the full tubes a more vigorous decomposition of the fat was to be expected.

It is evident that together with the fat-splitting, oxidation of the fatty acids takes place.

The special products resulting at the culture method of EYKMAN are fatty acids, soaps, oxidation products of fatty acids, and compounds of these acids with lipase.

Katalase, produced by the bacteria, plays no part therein, neither could this be shown for oxidases, these enzymes exerting no action on the fat-layer in the gelatin.

The favourable influence of light on the decomposition of fat in presence of lipase may be demonstrated by exposing some fatted tubes containing lipase gelatin to the light and compare them with similar tubes kept dark, whilst for control, tubes without lipase were exposed to the light and others kept out of it.

In the tubes containing gelatine with lipase and exposed to the light the fat is more strongly affected than in those prevented from it; the tubes acted upon by light and oxygen are most vigorously attacked.

In the tubes containing gelatin without lipase a slight decomposition of the fat is observed but it is inferior to that of the tubes with gelatin and lipase.

Synthesis of fat from glycerine and fatty acid by microbic lipase.

This lipase, as we have seen, splits fat in glycerine and fatty acid in presence of much water; it is able from glycerine and fatty acid again to build up fat, if very little water is present.

Some material of *B. lipolyticum* α was used as a lipase preparation.

These bacteria had been cultivated on broth-agar and after 10 days at 30° C. been taken off the agar with a spatule.

In this way about four and a half c.c. material had been procured.

This lipase preparation was introduced into a stoppered bottle with ± 50 c.c. oleic acid and ± 60 c.c. glycerine (S. W. 1.25), and after addition of a few glass beads for better mixing, the bottle was filled with glycerine, for which about 25 c.c. sufficed.

After the contents of the bottle had been rendered as homogeneous as possible by vivid shaking, 5 c.c. were withdrawn from it and supplied by 5 c.c. glycerine. These 5 c.c. oleic acid + glycerine titrated 77.2 c.c. $^1/_{10}$ N. caustic soda.

The bottle was now heated to 40° and remained 48 hours at this temperature, being during that time repeatedly and vividly shaken.

5 c.c. of the contents of the bottle then titrated 56.2 c.c. $^1/_{10}$ N caustic soda so that about $^1/_3$ of the oleic acid had disappeared.

The liquid was subsequently poured into two L. of boiling water and shaken with it, whereupon the oily layer was separated from it. The oily liquid was washed with hot water and shaken with a $^1/_2\,^0/_0$ natriumcarbonate solution by which the still present oleic acid dissolved into natriumoleate.

The remaining liquid was mixed with calciumcarbonate, heated to ± 200° C., then sucked off.

After this treatment 11.5 c.c. liquid was obtained of an oily consistency and yellow colour. It reacted neutrally as to litmus and was soluble in ether, benzene and carbon disulphide.

By heating with alcoholic kali saponification took place. A gram of this compound uses 163 mG. of KOH.

The S.W. amounted to 0.938.

Evidently in this synthesis the monoglyceride of oleic acid is chiefly formed, as follows from the S.W. and the saponification number; at the same time slight quantities of di- and tri-glycerides are present

Summary.

1. The composition of the medium is of no consequence for the secretion of lipase by microbes; so that every source of carbon or nitrogen, assimilated by a fat-splitting organism, will serve equally well for the production of lipase by this organism.

2. The secretion of acids by microbes in a culture medium diminishes the secretion of lipase.

3. Acids form compounds with lipase from which lipase is again freed by bases. The acid-lipases diffuse like lipase through gelatin and agar culture media; acid-lipases of higher fatty acids do not diffuse; acid-lipases do not decompose fat.

4. Hydrogenions retard, hydroxylions accelerate the action of lipase. If the acid degree of a medium exceeds $^1/_{50}$ N no more fat-splitting by lipase takes place. Lipase behaves to acids as a feeble basis.

5. Calcium- and magnesium-ions favour the action of lipase; likewise trimethylamine and natriumglycocholate; monovalent alcohols counteract the process, sugars and glycerine exerting no influence.

6. Presence of oxygen and light favour the decomposition of fat by the action of lipase.

7. By means of microbic lipase fat may be synthetically obtained. From oleic acid and glycerine chiefly the monoglyceride results but besides, probably a little di- and triglyceride.

8. Microbic lipase shows great similarity to liver- and pancreatic lipase.

Physics. — *"On the value of the critical quantities"*. By Prof. Dr. J. D. VAN DER WAALS.

(Communicated in the meeting of March 25, 1911).

Originally by the term *critical quantities* we understood the volume, the pressure, and the temperature of the critical point. For the value of these three quantities $v_k = 3b_g$, $p_k = \frac{1}{27}\frac{a}{b_g^2}$, and $RT_k = \frac{8}{27}\frac{a}{b_g}$ has been derived. But in the determination of these values it has been supposed that the quantity b, which had proved to be variable with the volume, would have changed only so little in the critical point that it might be put equal to the value which it has in infinitely large volume, and which will be denoted by the symbol b_g. But this equation $b_k = b_g$ implied at the same time the neglect of $\left(\frac{db}{dv}\right)_k$ and of $\left(\frac{d^2b}{dv^2}\right)_k$. In course of time the value of other quantities, as they appeared to be in the critical point, have come to the foreground.

In my communication on Quasi association (These Proc. XIII p. 107) I have mentioned $\frac{p_k v_k}{RT_k} = \frac{1}{s}$, $\frac{RT_k}{p_k} = r\,s\,b_g$, $\left(\frac{T}{p}\frac{dp}{dT}\right)_k = f$, $\frac{a}{v_k RT_k} = \frac{f-1}{s}$, and $\left(\frac{v}{v-k}\right)_k = \frac{f}{s}$, which together with the above three quantities $v_k = rb_g$ and $p_k = \frac{a}{b_g^2}\frac{1}{(f-1)r^2}$ and $RT_k = \frac{a}{b_g}\frac{sr}{(f-1)\,r^2}$, forms a number of 8 quantities, which, however, are not independent of each other. If the quantities a and b_g are determined by the choice of the substance, the knowledge of 3 quantities, viz. r, s, and f is sufficient to calculate them all.

From the property of the critical point follows that it is that point of the isothermic line for which the quantities $\left(\frac{dp}{dv}\right)_T$ and $\left(\frac{d^2p}{dv^2}\right)_T$ are equal to 0. So two equations must suffice for the determination. By means of these two equations the quantities v_k and RT_k are determined, and further the value of p_k by means of the equation for p itself. Also the other critical quantities mentioned are then derived by simple mathematical operations. If we put for p:

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

the two equations for the determination of v_k and RT_k are:

$$\left(\frac{dp}{dv}\right) = 0 = \frac{RT\left(1-\frac{db}{dv}\right)}{(v-b)^2} - \frac{2a}{v^3} \quad . \quad . \quad . \quad . \quad \text{(I)}$$

and from the differentiation of I and after elimination of RT:

$$\frac{v}{v-b}\left(1-\frac{db}{dv}\right) + \frac{\frac{v}{2}\frac{d^2b}{dv^2}}{1-\frac{db}{dv}} = \frac{3}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(II)}$$

If b was known as function of v, II might serve for the determination of v_k, and by means of this I might yield the value of RT_k. If for all substances a same function $\frac{b}{b_g} = f\left(\frac{b_g}{v}\right)$ existed, the same value would always be found for $\frac{b_g}{v_k}$ from II. In other words the quantity r in $v_k = rb_g$ would have the same value for all substances. But then RT_k would be an equally great fraction of $\frac{a}{b_g}$ for all substances, and p_k an equally great fraction of $\frac{a}{b_g{}^2}$. In the same way $\left(\frac{pv}{RT}\right) = \frac{1}{s}$ would have the same value for all substances — and particularly the investigations of Sydney Young show us that great differences exist in the value of s for the different substances. So we are compelled to abandon the assumption that in $\frac{b}{b_g} = f\left(\frac{b_g}{v}\right)$ the course of $\frac{b}{b_g}$ would be the same for all substances. It is clear that this brings the question what may be the cause of the circumstance that b becomes smaller with decreasing volume, to the front again, but for the moment I shall pass over this question in silence. That the value of $r = \frac{v_k}{b_g}$ is smaller than 3, and can be different for the different substances, I shall, however, assume as certain. And in the same way that r descends the more below 3 as b descends more rapidly with v. If we assume a real diminution of the molecule as cause of this variability of b with v, we might put this as follows: the quantity r is the smaller in the critical state as the molecule is the more compressible.

But whatever may be the cause of the variability of b, the law of this change is unknown, and the quantities $\frac{db}{dv}$ and $\frac{v}{2}\frac{d^2b}{dv^2}$, which occur in the equations I and II, are unknown. This excludes the possibility to make these equations serve for a determination of $\frac{v_k}{b_q}$ and of RT_k. Reversely, however, they can serve to determine $\frac{db}{dv}$ and $\frac{v}{2}\frac{d^2b}{dv^2}$ for the critical point, if v and RT_k are known in another way. In consequence of the disappearance of two equations which might serve for the determination of $\frac{v_k}{b_q}$ and RT_k, we must seek two new quantities which might serve us for this purpose, to which the circumstance is added, that now the equality of $b_k = b_q$ also disappears. Hence the knowledge of the 3 quantities v, f, and s is necessary for the determination of the critical data.

I shall assume the equation of p in the simplest form, viz.:

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

only with the addition that b depends on v. But I shall assume dependence on T neither of a nor of b. In my investigation, entitled: "Quasi association" it has been demonstrated that such a dependence on T cannot serve to account for the differences with the experiment, but that only the hypothesis of association can effect this. This removes the necessity of the assumption that a and b should be temperature functions. But of course this does not refute the possibility for such a dependence. Here I will investigate, however, in how far the results, obtained on the most simple suppositions, accord with the experiment, and not introduce again an unknown dependence, e.g. of b with T, which would, of course, render the derivation of a definite numerical value, impossible. In my "Quasi association" I have demonstrated that it is probably not of influence for the critical quantities in the shape to which I then reduced them, except for the quantity $\frac{v}{v-b} = \frac{f}{s}$ in a slight degree. The influence of quasi association on the value of the critical quantities being so slight, I shall neglect the quasi association for the sake of simplicity in the derivation of the relations which exist between the critical quantities, either accurate or by approximation. I shall only calculate at the end the extent of the deviations which are the consequence of this association.

Differentiating the equation for p with respect to T, keeping v constant, we find $\left(\frac{dp}{RT}\right)_v = \frac{R}{v-b}$ or $T\left(\frac{dp}{RT}\right)_v = \frac{RT}{v-b} = p + \frac{a}{v^2}$; and as

$\left(\frac{dp}{dT}\right)_v = \left(\frac{dp}{dT}\right)_{kr}$ in the critical point, we get:

$$T\left(\frac{dp}{dT}\right)_{kr} - p = \frac{a}{v^2}\,.$$

In this last equation $\left(\frac{dp}{dT}\right)_{kr}$ represents the increase of tension of the saturate vapour, as it is at the critical temperature. We may also write:

$$\left(\frac{T}{p}\frac{dp}{dT}\right)_{kr} - 1 = \frac{a}{p_k v_k^2}$$

or

$$p_k = \frac{a}{v_k^2\left[\frac{T}{p}\frac{dT}{dp} - 1\right]_{kr}}.$$

And putting $v_k = r b_g$

$$p_k = \frac{a}{b_g^2}\,\frac{1}{r^2\left[\frac{T}{p}\frac{dp}{dT} - 1\right]_{kr}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

For a number of substances the tension of the saturate vapour has been experimentally determined up to T_k — and especially the values of p for some thirty substances have been given by **Sydney Young** in "The Scientific Proceedings of the Royal Dublin Society" (June 1910). These tensions have been determined for temperatures between T_k and about $\frac{1}{2}$ T_k.

By approximation they are indicated by the empirical formula:

$$-\,Nep\;log\,\frac{p}{p_k} = f\,\frac{T_k - T}{T}$$

or

$$-\,Nep\;log\,\pi = f\,\frac{1-m}{m}\,.$$

But the quantity f is somewhat variable with m; starting from T_k or $m = 1$ there seems to be at first some diminution of f with descending value of m, which, however, has already been replaced by a rise for $m < \frac{1}{2}$, while for $m = \frac{1}{2}$ the value of m has again risen above f_{kr}. For still smaller value of m the observation is prevented by the appearance of the solid state. From some phenomena I have concluded as probable that e.g. at $f_k = 7$ the limiting value of f would rise to about 9 at the absolute zero.

From this empirical formula we derive:

$$\frac{d\pi}{\pi dm} = -\frac{f_m}{m^2} + \frac{1-m}{m}\frac{df_m}{dm}$$

or

$$\frac{m d\pi}{\pi dm} = \frac{f_m}{m} - (1-m)\frac{df_m}{dm},$$

and so

$$\left(\frac{m}{\pi}\frac{d\pi}{dm}\right)_{kr} = f_k.$$

If we wish to determine the value of f_k perfectly accurately, we are confronted, even with SYDNEY YOUNG's determinations, by difficulties. SYDNEY YOUNG represents the form of p by the formula of BIOT, viz. $Log\, p = a + ba^T + c\beta^t$; on the whole he succeeds in determining the many constants occurring in the formula so that the agreement with the experimental data is very satisfactory. But though we confine ourselves to the socalled normal substances — so excluding acetic acid and the alcohols — yet appreciable differences occur, especially in the neighbourhood of T_k. Differences great enough to be of importance for the value of $\left(\frac{md\pi}{\pi dm}\right)_{kr}$ which is to be calculated. A very elaborate investigation would be required to determine the most probable value of f_k. And perhaps the most reliable method for the calculation of this quantity is the direct one; viz. by reading as well $d\pi$ as dm and π and m at temperatures near T_k from the table of the observations. As an example I calculate for ethyl-acetate from:

p	T
26740	245
27535	247
28370	249
28800	250
28877	250,1

From the two first observations follows for $\frac{Tdp}{pdT}$ or $\frac{md\pi}{\pi dm}$ the value $\frac{795 \times 519}{27137 \times 2} = 7{,}6$. From the 3rd and 4th observation $\frac{430 \times 522{,}5}{28585} = 7{,}86$, while the difference of the temperatures is too slight for the calculation from the two last observations. The rise of p, which per degree is equal to 395 at $T=246$, and to 430 at $T=249{,}5$, would namely suddenly be equal to 770 at 250,05. Thus much we shall no doubt be able to conclude that f_k will not differ much from 7,6 or 7,8 for ethyl-acetate. I have thought I ought to call attention to this uncertainty of the absolutely accurate value of f_k, as we shall presently subject a probable relation between the values of some critical quantities to an investigation.

Let us now proceed to derive a value for RT_k. We do this by the aid of the value of what is often called "critical coefficient", which is also to be derived from the determinations of SYDNEY YOUNG and given by himself; viz. the quantity s from the relation:

$$\frac{RT_k}{p_k v_k} = s.$$

The uncertainty which exists in this quantity s is for the greater part the consequence of the uncertainty in the value of v_k. In most cases v_k was not directly determined, but calculated from the course of the value of liquid- and vapour volume at temperatures near T_k. This can be done with the aid of the law of the rectilinear diameter, or by applying the criterion $\left(\frac{dp}{dT}\right)_s = \left(\frac{dp}{dT}\right)_{kr}$. For RT_k we find now the value:

$$RT_k = \frac{a}{b_g} \frac{sr}{(f_k - 1) r^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II)$$

Eliminating b_g and r, we find from equations (I) and (II):

$$\frac{(RT_k)^2}{p_k} = a \frac{s^2}{f-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (III)$$

In my Quasi-association (These Proc. June 1910) I pronounced the expectation that at least approximately the factor of a, viz. $\frac{s^2}{f-1}$ would always have the same value for all normal substances, whatever might be the law of variability for the quantity b. I have since been strengthened in this opinion by the investigation of the value of $\frac{s^2}{f-1}$ for all normal substances, for which the quantities s and f have been determined experimentally.

If b does not vary with v, the value of $\frac{s^2}{f-1}$ is equal to $\frac{64}{27}$, and so we have to examine if $\frac{s^2}{f-1}$ is always found equal to this value.

In order to investigate the correctness or incorrectness of this relation as impartially as possible, I have taken the values for s and f which are given by KUENEN (Die Zustandsgleichung etc.), and then calculated s from:

$$s = \sqrt{\frac{64}{27}(f-1)}$$

and compared this value with the given one. The values of f occur on p. 142 and those for s on p. 60. KUENEN's numerical values, however, have been chosen so as to belong to the equation:

$$-\log_{10} \pi = f' \frac{1-m}{m}$$

and so to yield the values of f meant in the formula $\frac{s^2}{f-1} = \frac{64}{27}$ KUENEN's values must be divided by 0,4343.

	f'	f	s calculated	s given	
H_2	2.10	4.835	3.01	2.94	(?)[1]
Argon	2.18	5.02	3.08	2.67	
O_2	2.50	5.757	3.36	3.49	(?)
Ethylene	2.75	6.33	3.55	3.42	
CO_2	2 86	6.58	3.636	3.59	
Ethane	2.60	6	3.443	3.55	
CCl_4	2.81	6.47	3.606	3.67	
Benzene	2.89	6.65	3.67	3.75	
Fluor-benzene	2.99	6.885	3.735	3.78	
Ether	3.01	6.93	3.75	3.81	
Esters	2.97—3.25	6.84—7.48	3.715—3.92	3.86—3.94	

First of all in this table the great difference in calculated and given value of s for Argon is very striking — and this led me to inquire into the cause for this great difference. Now before the appearance of the Proceedings of the Royal Society of Febr. 1911 I happened to look through the proof, and in this way I got acquainted with the observations of KAMERLINGH ONNES and CROMMELIN, who give values for f' and s for Argon. There the value 3,283 is given for s, so still greater than in KUENEN's list. But on the other hand f' is much greater than is given above. If we take the value of f' at $t = -125{,}49$, viz. 2.577, then $f = 5.934$, and we calculate $s = 3.41$; — again appreciably greater than 3,283. This led me to calculate the value of f_k itself from the data occurring in the cited communication. Specially because a sudden increase takes place in the given value of f' near the critical temperature, which is not the case for other substances to the same extent. Between $t = -140.80$ and $t = -125.49$ KAMERLINGH ONNES and CROMMELIN give four values for f' for ascending temperatures, viz. 2.415, 2.421, 2.457, and finally 2.577. The last value I have re-calculated — and I come

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[1] The (?) mark is KUENEN's.

to the conclusion that it is too large. In two ways I have tried to determine f' and so also f. First of all by taking Δp, ΔT and p and T between the two highest temperatures, and substituting into the formula $f = \frac{T\Delta p}{p\Delta T}$. We find $\Delta p = 6.611$, $\Delta T = 4.34$, $p = 39{,}1515$ and $T = 145.34$ and from this $f = 5.66$ — and in the second place by calculating f' from $-\log_{10}\frac{p}{p_k} = f'\frac{T_k - T}{T}$. Then we find $f' = 2.425$ and $f = 5.6$. So the sudden increase in the value of f' does not exist. With $f = 5.6$ we calculate $s = 3.29$ — which lies exceedingly near the value 3.283 found.

So in this case we have an almost perfect harmony between the formula which supposes $\frac{s^2}{f-1} = \frac{64}{27}$, and the observation for a substance with very low critical temperature. For one with a high value of s, viz. ethyl-acetate, for which $s = 3.949$ is put by SYDNEY YOUNG, we get as good an agreement if we put f between 7.6 and 7.8, as was found above (p. 1215). With $f = 7.7$ we find $s = 3.977$, while SYDNEY YOUNG gives $s = 3.949$.

Only for helium a very great divergence would be found. In the paper already mentioned in the discussion of Argon $s = \frac{8}{3}$ is put for helium. To this corresponds $f = 4$ or $f' = 1.7372$ — while $f' = 1.2$ is given as highest value. But then $f = 4$ is the lowest value for f, which is possible according to the equation of state — unless we should accept the perfectly inconceivable supposition that b increases with v.

If we examine the validity of the relation $\frac{s^2}{f-1} = \frac{64}{27} = 2.37$ for the alcohols and acetic acid according to the observations of SYDNEY YOUNG, we are in the first place struck with the difficulty to derive the value of f_k with any certainty from the observations. For methyl-alcohol there is at the higher temperatures generally a great difference between the observations and the formula of BIOT used by SYDNEY YOUNG — differences which irregularly change their signs at temperatures which differ only 1 or $^1/_2$ degree. As probable value of f_k I have chosen 8.35. If the said relation between s and f existed, $s = 4.17$ would correspond to this, while SYDNEY YOUNG gives $s = 4.559$. For methyl-alcohol the same difficulty in the determination of f_k holds, for this substance I think I have to assume the value 8.5. According to the above relation $s = 4.215$ would correspond to this, while Sydney Young gives the value 4.26 for s. For propylalcohol I have chosen f_k equal to 7.78, which differs greatly from Kuenen's value 3.93. The value thought probable by me agrees almost entirely with 3.39 instead with 3,93. According to the above relation $s = 4$ corresponds to it, while Sydney Young gives $s = 3{,}998$. So tested by the above relation propyl-alcohol would already be a normal substance. But for acetic acid, for which at low temperatures the saturate vapour already consists almost entirely of double molecules, the relation does not hold at all.

If it is taken into consideration that the values of f, printed unmodified in the above table are mean values, which may only accidentally be the values of f_k — I feel justified in assuming that for normal substances $\frac{s^2}{f-1} = \frac{64}{27}$ may be considered as valid at least to a high degree of approximation. Accordingly I harbour the expectation that further investigation will make the exception for helium disappear. If, however, this small value of f is found confirmed on further investigation, helium would have to be called a very abnormal substance.

So the quantity a is determined from T_k and p_k by the relations already given in my Thesis for the doctorate, at least to a high degree of approximation.

In my Quasi-association I had arrived at this relation through the assumption that in the critical point two quantities would have the same values as follows from the assumption $b =$ constant, viz. $sr = 8$ and $(f-1)r^2 = 27$. Then $s^2r^2 = 64$ and after elimination of r we get the equation $\frac{s^2}{f-1} = \frac{64}{27}$. But the equation obtained after elimination of r can be valid without sr and $(f-1)r^2$ being constant. Thus e.g. with $sr = 7{,}5$ and $(f-1)r^2 = 23{,}34$ the same relation between s and f can be refound. So the question is now whether both relations ($sr = 8$ and $(f-1)r^2 = 27$) may be considered as valid to a high degree of approximation. As v_k could indeed be determined experimentally, but not $r = \frac{v_k}{b_g}$, I had arrived at the supposition $sr=8$ and $(f-1)r^2=27$, by assuming a value for r which could not be far from the correct one.

I have tried to determine what would follow for different properties of the quantities in the critical point if the two relations mentioned should be perfectly accurate, viz. 1. For the quantity $\frac{b_k}{bg}$, 2 the quantity $\left(\frac{db}{dv}\right)_k$, and 3 the quantity $\left(\frac{v}{2}\frac{d^2b}{dv^2}\right)_k$.

1. The quantity $\frac{b_k}{bg}$ is found by determining $\left(T\frac{dp}{dT}\right)_k$: equal to $f = \frac{1}{p}\frac{RT}{(v-b)_k}$, or $\frac{f}{s} = \frac{v}{(v-b)_k} = \frac{r}{r-\frac{b_k}{bg}}$, from which follows:

$$\frac{b}{bg} = r\left(1-\frac{s}{f}\right).$$

With $rs = 8$, we should find:

$$\frac{b}{bg} = r - \frac{8}{f}.$$

I shall, however, not at once suppose $rs = 8$, nor $(f-1)\,r^2 = 27$, but assume $rs = c_1$, and $(f-1)\,r^2 = c_2$, and c_1 and c_2 to be variable with r. Differentiating the relation:

$$\frac{b}{bg} = r - \frac{rs}{f} = r - \frac{c_1}{f} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (IV)$$

with respect to r we get, because bg does not depend on r:

$$\frac{db}{bg\,dr} = 1 + \frac{c_1}{f^2}\frac{df}{dr} - \frac{1}{f}\frac{dc_1}{dr}$$

or

$$\frac{db_k}{dr_k} = 1 + \frac{c_1}{f^2}\frac{df}{dr} - \frac{1}{f}\frac{dc_1}{dr}$$

From $(f-1)\,r^2 = c_2$ follows $\frac{1}{f-1}\frac{df}{dr} + \frac{2}{r} = \frac{dc_2}{c_2dr}$, in consequence of which we get:

$$\frac{db_k}{dv_k} = 1 - \frac{2s\,(f-1)}{f^2} + \frac{c_1\,(f-1)}{f^2}\frac{dc_2}{c_2dr} - \frac{1}{f}\frac{dc_1}{dr}.$$

And by means of the relation $\frac{c_1^{\,2}}{c_2} = \frac{s^2}{f-1} = \text{constant}$, or

$$2\frac{dc_1}{c_1} = \frac{dc_2}{c_2}$$

finally:

$$\frac{db_k}{dv_k} = 1 - \frac{2s\,(f-1)}{f^2} + \frac{dc_1}{dr}\frac{f-2}{f^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (V)$$

The equation (IV) gives us the fraction which in the critical point is the quantity b of bg. It appears, as was to be expected, to be dependent on the value of r for this point. If rs should always be equal to 8, and $(f-1)\,r^2 = 27$, this fraction would be determined by r and depend on it in the following way:

$$\frac{b}{b_g} = r - \frac{8}{1 + \frac{27}{r^2}}\,.$$

For $r = 3$, the greatest value which r can assume, we find $\frac{b}{b_g} = 1$, as was to be expected. But though this quantity decreases with the decrease of r, as was to be expected, this decrease is slight; thus with $r = 2$ the value of $\frac{b}{b_g} = \frac{30}{31}$.

Equation (V), derived from (IV), reveals the direction of the tangent to the locus (IV), and for the case that sr would always be equal to 8, it yields for $\frac{d\left(\frac{b}{b_g}\right)}{dr}$ the value:

$$1 - \frac{2s\,(f-1)}{f^2}$$

which for $s = \frac{8}{3}$ and $f = 4$ is equal to 0, for $s = 3{,}77$ and $f = 7$ to $\frac{3.76}{49}$, and for $s = 4$ and $f = \frac{31}{4}$ to $\frac{97}{961}$.

2. The quantity $\left(\frac{db}{dv}\right)_{kr}$. This quantity is found from the condition that $\left(\frac{dp}{dv}\right)_T$ must be equal to 0 in the critical point.

From $\left(\frac{dp}{dv}\right)_T = 0$, we find:

$$\frac{RT\left(1 - \frac{db}{dv}\right)}{(v-b)^2} = \frac{2a}{v^3}$$

or

$$1 - \left(\frac{db}{dv}\right)_{kr} = \frac{2a}{v_k R T_k}\left(\frac{v-b}{v}\right)^2_{kr}\,.$$

And substituting the value $\frac{a}{v_k R T_k} = \frac{f-1}{s}$ and $\left(\frac{v-b}{v}\right)_{kr} = \frac{s}{f}$, in it, which values already occur in my paper on quasi association, we find:

$$1-\left(\frac{db}{dv}\right)=\frac{2s\,(f-1)}{f^2}\quad . \; . \; . \; . \; . \; . \; . \quad (VI)$$

Comparing this value with (V) we see that if c_1 should be independent of v, and so $c_1 = sr$ always strictly equal to 8, the value of $\left(\frac{db}{dv}\right)_{kr}$ would be perfectly the same as $\frac{db_k}{dv_k}$. But these two quantities do not mean the same thing. The meaning of what I have represented by $\left(\frac{db}{dv}\right)_{kr}$ is clear. We have a substance with definite a and b_g. The quantity b, which is only equal to b_g for infinitely large volume, decreases on decrease of the volume, whatever may be its cause and the law according to which it decreases. Starting from very large volume, the decrease is so small at first that it can practically be neglected, and $\frac{db}{dv}$ may be put almost equal to 0. I have represented the value which $\frac{db}{dv}$ has in the critical point, by $\left(\frac{db}{dv}\right)_{kr}$.

The way in which, even for substances with the same value of b_g, the quantity b depends on v appears to be different, and this circumstance calls up the question again, what is, after all, the cause of this variability of b. At the critical point $\frac{b}{b_g}$, $\frac{db}{dv}$, and as we shall more fully discuss later on $\frac{d^2b}{dv^2}$, are very different. And the different way in which b depends on v, is the cause, that the quantities s, f and r differ in the critical point.

But the significance of $\frac{d\left(\frac{b}{b_g}\right)}{dr}$, which quantity I have represented in (V) by $\frac{db_k}{dv_k}$, is another. The equation (IV), from which it has been derived, viz. $\frac{b_k}{b_g}=r-\frac{c_1}{f}=r\left(1-\frac{s}{f}\right)$ enables us to calculate $\frac{b}{b_g}$ in the critical point, when r, s and f should be known for a substance, and may therefore be considered as a locus holding for all substances, whatever may be the law of dependence of b with v. So it does not belong to a single substance. If the dependence of b with v is given, only a single point of this locus refers to this substance, viz. that point in which $\frac{b}{b_g}=f\,(v)$ for that definite substance intersects the locus. And if we knew this locus perfectly, and also the value of $\frac{b}{b_g}$ for that definite substance, we could determine the critical point by determining where $\frac{b}{b_g}$ intersects the given locus. For greater values of r the curve $\frac{b}{b_g}$ for the definite substance lies below the locus, and for smaller value of r above it. And it follows already from this that $\left(\frac{db}{dv}\right)_{kr}$ must be smaller than $\frac{db_k}{dv_k}$, or $1-\left(\frac{db}{dv}\right)_{kr} > 1-\frac{db_k}{dv_k}$.

Then it follows by comparison of (V) with (VI) that $\frac{dc_1}{dr}$ must be positive. This means that sr is equal to 8 only for $r=3$, or for constant value of b; but in all other cases, so if b decreases with v, it is smaller than 8, and the more so as the variability of b is stronger.

Now the value of the factor of $\frac{a}{b_g}$ for RT_k does not only depend on sr. This factor is $\frac{rs}{(f-1)\,r^2}$ or $\frac{c_1}{c_2}$. Representing this factor by F, we get $\frac{dF}{Fdr}=\frac{dc_1}{c_1dr}-\frac{dc_2}{c_2dr}$. And $\frac{c_1{}^2}{c_2}$ being constant, $2\,\frac{dc_1}{c_1dr}=\frac{dc_2}{c_2dr}$. Hence $\frac{dF}{Fdr}=-\frac{dc_1}{c_1dr}$. To find this result, we might also have written the factor of $\frac{a}{b_g}$: $\frac{(rs)^2}{(f-1)r^2}\,\frac{1}{rs}$ or $\frac{64}{27}\,\frac{1}{rs}$. So if for all substances for which b is variable with v $rs<8$, then $RT_k>\frac{8}{27}\,\frac{a}{b_g}$ and this result might also have been arrived at in a simpler way.

Let us imagine for this purpose two substances with given a and b_g — the former with constant b, the latter with b decreasing with diminishing v. If for given value of T we plot an isotherm for both substances — we see at once that the isotherm for the second substance will always lie below that of the first substance. As for every value of v the quantity $v-b$ is greater for the second substance than for the first, $\frac{RT}{v-b}$ is smaller for the first substance than for the second, and $\frac{a}{v^2}$ being the same for the two substances, $p_2<p_1$. For

great volumes b for the second substance is only very slightly smaller than b_g, and for great volumes the two isotherms may almost be considered as coinciding. But still, the fact remains that there is a difference, and that this difference increases with decrease of volume, and that this difference is the greater as the variability of b is more pronounced.

At a value of v, for which $\frac{dp}{dv} = 0$ in the isotherm which lies above the other, $\frac{dp}{dv}$ is positive in the lower isotherm. So the limits for the unstable region are further apart in this case than for the upper isotherm. But the displacement of these limits is more considerable on the side of the small volumes. At the critical temperature of the first substance, so at $RT_k = \frac{8}{27}\frac{b}{bg}$, $\frac{dp}{dv}$ will still be positive for $v = 3bg$ for the second substance, and so the temperatures will still have to rise, and become greater than $\frac{8}{27}\frac{a}{bg}$, before the critical temperature of the second substance is reached.

But though we know that sr is smaller than 8 in all cases in which b becomes smaller at the same time with v, and the more so as b varies more rapidly with v, still we have no rule as yet to determine the value of this quantity. Of course, this would be the case, if the law of the variability of b was known.

For instance, if $\frac{b}{bg} = 1 - \alpha\frac{bg}{v}$ could be put, which might be done for not too small volumes, if the reason of the variability of b is not a real diminution of the molecule, but must be ascribed to an apparent diminution, as I already did in 1873. Then (IV) reduces to:

$$1 - \frac{\alpha}{r} = r - \frac{rs}{f}$$

and (VI) to:

$$1 - \frac{\alpha}{r^2} = \frac{2s\,(f-1)}{f^2}$$

and with elimination of α, the approximate equations to:

$$1 - \frac{1}{r} = \frac{2s\,(f-1)}{f^2} - 1 + \frac{s}{f}$$

or

$$\frac{1}{r} = 2 - \frac{3s}{f} + \frac{2s}{f^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (VII)$$

or

$$\frac{1}{sr} = \frac{2}{s} - \frac{3f-2}{f^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (VIII)$$

For $s = \frac{8}{3}$ and $f = 4$, we find of course again $sr = 8$, but to this a value of $a = 0$ belongs. With $s = 3{,}64$ and $f = 6{,}6$ we find for CO_2 the value $sr = 7{,}1$, which value is smaller than I had expected. For ether, for which we may put $s = 3{,}77$ and $f = 7$, we find sr little different from 7,1. Small errors in r and f, however, have a great influence on the value of this quantity. For r a value is found little higher than 1,88. That in my "Quasi association" I put sr little different from 8 also for substances like ether is, therefore owing to a too high value for r. If the value of a is calculated from $1 - \frac{a}{r} = r - \frac{rs}{f}$ or from $1 - \frac{a}{r^2} = \frac{2s(f-1)}{f^2}$, a is found to differ little from $^3/_8$. This result would be in perfect accordance with what the theory had predicted concerning the value of a in the approximate formula used for spherical molecules. But we find another value of a for another value of s and f.

The relation between a and f is given by the formula:

$$a\frac{1}{r^2} = 1 - \frac{2s(f-1)}{f^2}$$

and by the aid of (VII)

$$a \left\{ 2 - s\frac{3f-2}{f^2} \right\}^2 = 1 - \frac{2s(f-1)}{f^2}$$

from which we derive:

$$\frac{f^2}{s}\frac{da}{df} = (f-2)\frac{-\frac{1}{f-1} + \frac{s}{f^2}\left(3 - \frac{4}{f^2}\right)}{\left(2 - s\frac{3f-2}{f^2}\right)^3}$$

This value of $\frac{da}{df}$ is equal to 0 for $f = 4$ and $s = \frac{8}{3}$, but for greater value of f and corresponding value of s it is always positive, as, indeed, might have been expected. It was, namely, to different variability of b with v that we attributed the different value of f and s. But the different value of a is still inexplicable. Is the deviation from the spherical shape the cause? And is, for the cases in which $a > \frac{3}{8}$, another cause, a real diminution of the molecule added to the cause assumed up to now for the decrease of b? But the assumption :

$$\frac{b}{b_g} = 1 - \alpha \frac{b_g}{v}$$

becomes altogether improbable by the consideration of the value of $\frac{d^2b}{dv^2}$.

3. The quantity $\left(\frac{v}{2}\frac{d^2b}{dv^2}\right)_{kr}$. This quantity is found from the condition that $\left(\frac{d^2p}{dv^2}\right)_T$ is $= 0$ in the critical point.

Equation (II):

$$\frac{v}{v-b}\left(1-\frac{db}{dv}\right) + \frac{\frac{v}{2}\frac{d^2b}{dv^2}}{1-\frac{db}{dv}} = \frac{3}{2}$$

yields for the value of $\frac{v}{2}\frac{d^2b}{dv^2}$, if we put $\frac{v}{v-b} = \frac{f}{s}$ and $\left(1-\frac{db}{dv}\right) = = \frac{2s(f-1)}{f^2}$:

$$-\left(\frac{v}{2}\frac{d^2b}{dv^2}\right)_{kr} = \frac{s(f-1)(f-4)}{f^3} \quad . \quad . \quad . \quad . \quad . \quad (IX)$$

For $f = 4$ we find this value again equal to 0. For $f = 7$ and $s = 3.78$ the value is equal to $0.54 \times \frac{18}{49}$ or nearly 0,2.

The equation (IX) can be derived from (VI) without it being necessary to have recourse to (II). Nor need (VI) be derived from (I). From the relation $\frac{b}{bg} = r - \frac{rs}{f}$ we could have found $\left(\frac{db}{dv}\right)_{kr}$ from v by keeping c_1 constant as should be done for a constant substance. Then we get:

$$1 - \frac{db}{dv} = \frac{2s(f-1)}{f^2}$$

and by differentiation of this equation, keeping c_2 constant:

$$-\frac{d^2b}{dv^2}dv = 2ds\frac{f-1}{f^2} + 2s\left(-\frac{1}{f^2}+\frac{2}{f^3}\right)df$$

or

$$-\left(v\frac{d^2b}{dv^2}\right)\frac{dv}{v} = \frac{s}{f^2}\left\{2\frac{ds}{s}(f-1) + 2\left(-1+\frac{2}{f}\right)d\right\}.$$

Writing $\frac{dr}{r}$ for $\frac{dv}{v}$, and df for $2\frac{ds}{s}(f-1)$, we find:

$$-\left(\frac{vd^2b}{dv^2}\right)_{kr} = \frac{r\,df}{dr}\,\frac{s}{f^2}\left\{1-2+\frac{4}{f}\right\} = \frac{rdf}{dr}\,\frac{s}{f^3}\,(-f+4),$$

and as $\frac{df}{f-1}+\frac{2dr}{r}=0$:

$$-\left(\frac{v}{2}\,\frac{d^2b}{dv^2}\right)_{kr} = \frac{s(f-1)\,(f-4)}{f^3},$$

and

$$-\left(\frac{v}{2}\,\frac{d^2b}{dv^2}\right)_{kr} = \frac{f-4}{2f}\left(1-\frac{db}{dv}\right)_{kr}.$$

As $\left(1-\frac{db}{dv}\right)_{kr}$ differs little from 1, we have in $\frac{f-4}{2f}$ an approximate value for $-\left(\frac{v}{2}\,\frac{d^2v}{db^2}\right)_{kr}$.

The value of $-\left(\frac{v}{2}\,\frac{d^2b}{dv^2}\right)_{kr}$ is exceedingly great, in comparison with $\left(\frac{db}{dv}\right)_{kr}$, and this latter is again great in comparison with $1-\frac{b}{b_g}$. And that this could not be accounted for, if we put $\frac{b}{b_g}=1-\alpha\frac{b_g}{v}$, is particularly obvious if we compare $-\left(\frac{v}{2}\,\frac{d^2b}{dv^2}\right)_{kr}$ with $\left(\frac{db}{dv}\right)_{kr}$. Putting $\frac{b}{b_g}=1-\alpha\frac{b_g}{v}$, we find then $\left(\frac{db}{dv}\right)=\alpha\left(\frac{b_g}{v}\right)^2$, and in the same way $\left(-\frac{v}{2}\,\frac{d^2b}{dv^2}\right)=\alpha\left(\frac{b_g}{v}\right)^2$. The ratio of the two mentioned values would then be 1.

We might account for the high ratio between the two quantities by an equation of the following form:

$$\frac{b}{b_g}=1-\alpha\left(\frac{b_g}{v}\right)^n$$

Then $\frac{db}{dv}=n\alpha\left(\frac{b_g}{v}\right)^{n+1}$ and $\left(-\frac{v}{2}\,\frac{d^2b}{dv^2}\right)=\frac{n(n+1)\alpha}{2}\left(\frac{b_g}{v}\right)^{n+1}$, so that the ratio would be $\frac{n+1}{2}$. Then for the determination of n we have the equation:

$$\frac{n+1}{2}=\frac{\dfrac{s(f-1)\,(f-4)}{f^3}}{1-\dfrac{2s\,(f-1)}{f^2}}.$$

For $n=4$ and $s=\frac{8}{3}$ numerator and denominator are equal to 0, but this case supposes $b=b_g$. For $s=3.78$ and $f=7$ we should find:

$$n+1=\frac{1.08\times\frac{6}{7}\times\frac{3}{7}}{1-1.08\times\frac{6}{7}}=5.34$$

or

$$n=4.34$$

For the determination of r we have the equations:

$$\frac{b}{b_g}\frac{1}{r}=1-\frac{s}{f}$$

or

$$\frac{1-\frac{a}{r^n}}{r}=1-\frac{s}{f}$$

or

$$\frac{1}{r}=1-\frac{s}{f}+\frac{a}{r^{n+1}}=1-\frac{s}{f}+\frac{\frac{db}{dv}}{n}$$

or

$$\frac{1}{r}=1-\frac{s}{f}+\frac{1-\frac{2s(f-1)}{f^2}}{n}$$

For $s=3.78$ and $f=7$ and $n=4.34$, we find:

$$\frac{1}{r}=0{,}46+0{,}01713=0\ 47713$$

or

$$r=2{,}0957.$$

And this value of r is, indeed, smaller than the estimation in my "Quasi association", but only very little.

On the supposition that sr should always be equal to 8, we should find $r=2{,}116$ — so that the difference would hardly amount to 1 $^0/_0$. Hence we find $sr<8$, as was demonstrated above, but only little smaller, viz. 7,9217. And for $(f-1)\,r^2$ we do not find exactly 27, but a slightly smaller value, viz. 26,352. But the question what is, after all, the cause of the variability of b, is not answered yet, and

$\frac{b}{b_g} = 1 - \alpha \left(\frac{b_g}{v}\right)^n$ is to be considered only as an empirical formula, holding by approximation in the neighbourhood of v_k.

Now, however, it remains to investigate in how far the existence of Quasi association has influence on the obtained results.

In general:

$$\left(\frac{dp}{dT}\right)_v = \left(\frac{dp}{dT}\right)_{vx} + \left(\frac{dp}{dx}\right)_{vT} \left(\frac{dx}{dT}\right)_v.$$

And $\left(\frac{dp}{dT}\right)_v$ being equal to $\frac{dp}{dT}$ in the critical point, also:

$$T\frac{dp}{dT} = \frac{RT\left\{1 - \frac{n-1}{n}x\right\}}{v-b} + \left(\frac{dp}{dx}\right)_{vT}\left(T\frac{dx}{dT}\right)_v$$

or

$$T\frac{dp}{dT} - p = \frac{a\left(1-\frac{x}{2}\right)^2}{v^2} + \left(\frac{dp}{dx}\right)_{vT}\left(T\frac{dx}{dT}\right)_v.$$

Now we have chosen the quantity n so, that:

$$T\frac{dp}{dT} - p = \frac{a}{v^2}$$

or in such a way that:

$$\frac{a\left(x - \frac{x^1}{4}\right)}{v^2} = \left(\frac{dp}{dx}\right)_{vT}\left(T\frac{dx}{dT}\right)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

Now the value of $\left(\frac{dx}{dT}\right)_v$ is necessarily negative, and so the value of $\left(\frac{dp}{dx}\right)_{vT}$ will also be negative for the chosen value of n.

Though the ψ-surface has minimum value of T_k for a definite value of x, a section at given value of v will not begin with increase of p, as is usually the case; but will always show decreasing value of p. The value of $\left(T\frac{dx}{dT}\right)_v$ we must determine by differentiation of $\left(\frac{d\psi}{dx}\right)_{vT} = 0$ and so from the equation:

$$\left(\frac{d^2\psi}{dx\,dv}\right)_T dv + \left(\frac{d^2\psi}{dx^2}\right)_{vT} dx + \left(\frac{d^2\psi}{dx\,dT}\right)_v dT = 0$$

or

$$-\left(\frac{dp}{dx}\right)_{vT} dv + \left(\frac{d^2\psi}{dx^2}\right)_{vT} dx - \left(\frac{d\eta}{dx}\right)_{vT} dT = 0$$

or

$$-\left(\frac{dp}{dx}\right)_{vT} dv + \left(\frac{d^2\psi}{dx^2}\right)_{vT} dx - \left(\frac{d\varepsilon}{dx}\right)_{vT} \frac{dT}{T}$$

And as $\varepsilon = -Ex - \dfrac{a\left(1-\dfrac{x}{2}\right)^2}{v}$

$$-\left(\frac{dp}{dx}\right)_{vT} dv + \left(\frac{d^2\psi}{dx^2}\right)_{vT} dx + \left[E - \frac{a\left(1-\frac{x}{2}\right)}{v}\right]\frac{dT}{T} = 0$$

From this we find:

$$T\left(\frac{dx}{dT}\right)_v = -\frac{E - \dfrac{a\left(1-\dfrac{x}{2}\right)}{v}}{\left(\dfrac{d^2\psi}{dx^2}\right)_{vT}}.$$

The value of $\left(\dfrac{d^2\psi}{dx^2}\right)_{vT}$ I gave (These Proc. June 1910) in the form:

$$\left(\frac{d^2\psi}{dx^2}\right)_{vT} = RT\left\{\frac{1+(n-1)x}{nx(1-x)} - \frac{a}{2vRT}\right\}$$

But there has an error slipped in there, which is indeed without influence for small value of x, but which I must yet rectify. As this would here divert us from the question we are dealing with, I shall discuss the way in which the rectification is obtained, later on, and now only give the corrected value. We should find:

$$\left(\frac{d^2\psi}{dx^2}\right)_{vT} = RT\left\{\frac{1}{nn(1-x)\left(1-\dfrac{n-1}{n}x\right)} - \frac{a}{2vRT}\right\}$$

Substituting the value of $\left(T\dfrac{dx}{dT}\right)_v$ in equation (α) we find with a high degree of approximation (for small value of x):

$$1 = -v\left(\frac{dp}{dx}\right)_{vT} \frac{\left(E\dfrac{vk}{a} - 1\right)}{RT} n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\beta)$$

If we write the value of p in the following form:

$$p+\frac{a}{v^2}=\frac{RT\left(1-\frac{n-1}{n}\right)}{v-b}+\frac{a\left(x-\frac{x^2}{4}\right)}{v^2}$$

Bearing in mind that $p+\frac{a}{v^2}=T\frac{dp}{dT}$, we find for small value of x:

$$T\frac{dp}{dT}=\frac{RT}{v-b}+x\left(\frac{dp}{dx}\right)_{vT}$$

according to (β)

$$T\frac{dp}{dT}=\frac{RT}{v-b}-\frac{xRT}{v}\frac{1}{n\left(\frac{Ev_k}{a}-1\right)}$$

or dividing by p:

$$f=s\frac{v}{v-b}-s\frac{x}{n\left(\frac{Ev_k}{a}-1\right)}$$

So the value of $\frac{v}{v-b}$ is found to be somewhat greater than $\frac{f}{s}$, but so little that our foregoing calculations can remain unchanged.

Geophysics. — "*On tidal forces as determined by means of* WIECHERT's *astatic seismograph*". By Dr. C. BRAAK. (Communicated by Dr. VAN DER STOK.)

(Communicated in the meeting of March 25, 1911).

In a previous communication the E—W component of the semi-diurnal lunar tidal motion of the ground at Batavia, as deduced from registrations of WIECHERT's astatic seismograph during the period of July to December 1909, was stated to be:

$$0''.0114\ cos\ (2t-251^\circ\ 53')$$ [1],

whereas the theoretical value is:

$$0''.0155\ cos\ (2t-270^\circ)$$

The registrations obtained during the following half-year have now been worked out upon the same plan and, in addition to this tide, the other principal tides have been calculated for the whole period of one year, except the semi-diurnal solar tide, which is strongly disturbed by the diurnal heat wave.

These tides, enumerated according to their importance, are:

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[1] These Proceedings XIII. 1910, p. 17—21.

M_2,	semidiurnal lunar tide	E—W. component
K_1,	Sun's-moon's-declination tide	N—S. „
O,	Moon's declination tide	„ „
P,	Sun's declination tide	„ „
K_2,	Sun's-moon's declination tide	E—W. „
M_2,	semidiurnal lunar tide	N—S. „

As before, the semidiurnal tides were determined by first measuring off the distances between the registrations at 7^h and 10^h, 8^h and 12^h etc., and taking the differences (13—10)—(10—7) etc.

For the diurnal tides the same method was applied to the registrations at the hours 16^h and 10^h, 10^h and 4^h etc.

The sensitiveness was deduced by determining the period of vibration and the indicator-magnification, as explained in the former communication.

As the position of the instrument has not been altered, the former values:

234.3 (E—W) and 185.7 (N—S)

have been assumed for the indicator-magnification.

In the different months the following values were found for the mean times of vibration:

		E—W	N—S
1909	July	10.0^5	10.4
	Aug.	10.1	10.3
	Sept.	10.0	10.1
	Oct.	9.6	9.8
	Nov.	9.7	10.1
	Dec.	9.6^5	10.0
1910	Jan.	9.8	9.8
	Febr.	10.0^5	10.0^5
	March	9.5	9.5
	April	9.7	9.7
	May	9.5	9.5
	June	9.1	9.0^5

The equivalent pendulum-length as deduced from these data is:

E—W pendulum: 22.70 meters
N—S „ : 23.83 „

The variation of inclination corresponding with a deflection of 1 mm. in the diagram is accordingly:

for the E—W component: $0''.0388$
„ „ N—S component: $0''.0466$

As has been noticed in the previous communication the method followed of measuring off the distances mentioned above gives twice the amplitude multiplied by $1 - \cos 3a$ ($a =$ angular velocity per hour) for the semi-diurnal tides as the argument varies in 3 hours not 90°, but $3a$.

For the diurnal tides twice the amplitude multiplied by $1 - \cos 6a$ is obtained.

The deflections have been measured off corresponding to the time signal, given 5,5 minutes before Batavia time; the arguments have been corrected accordingly.

The values of the tides mentioned above as found by means of the records, and also their theoretical values on the assumption of an absolutely rigid earth, are:

July 1, 1909, noon.

M_2, E—W	observed value	$0''.01120 \cos (2t - 58^\circ.0)$ [1]
	theoretical ,,	$0''.01544 \cos (2t - 45^\circ.5)$
M_2, N—S	observed value	$0''.00848 \cos (2t - 356^\circ.9)$
	theoretical ,,	$0''.00167 \cos (2t - 315^\circ.5)$
K_2, E—W	observed value	$0''.00277 \cos (2t - 245^\circ.8)$
	theoretical ,,	$0''.00229 \cos (2t - 269^\circ.8)$
O, N—S	observed value	$0''.00644 \cos (t - 38^\circ.2)$
	theoretical ,,	$0''.00700 \cos (t - 312^\circ.8)$
K_1, N—S	observed value	$0''.00449 \cos (t - 313^\circ.6)$
	theoretical ,,	$0'',00945 \cos (t - 359^\circ.8)$
P, N—S	observed value	$0''.00645 \cos (t - 84^\circ.2)$
	theoretical ,,	$0''.00291 \cos (t - 9^\circ.2)$

North and West are reckoned positive; July 1, 1909, noon has been taken as the beginning of time-reckoning.

Although the E—W components, but for a somewhat excessive value of the K_2 amplitude, closely agree with the theoretical values, the N—S components on the contrary show considerable deviations. That this disagreement is not due to errors of the instrument is proved by the following values for the N—S component of the M_2 tide, calculated for each hour.

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[1] Owing to an error in the calculation, the difference between the observed and the theoretical values of the argument is not the same as that given in the earlier communication.

10^h $0.348\ cos\ (2t—170°.4)$
11 $0.334\ cos\ (2t—175°.1)$
12 $0.400\ cos\ (2t—177°.3)$
1 $0.346\ cos\ (2t—176°.5)$
2 $0.414\ cos\ (2t—178°.1)$
3 $0.392\ cos\ (2t—184°.2)$
4 $0.420\ cos\ (2t—183°.0)$
5 $0.367\ cos\ (2t—192°.4)$

For the N—S component of the O-tide, we found, taking together two consecutive hours:

10 and 11 hour $0.123\ cos\ (t—199°.2)$
12 ,, 1 ,, $0.199\ cos\ (t—229°.6)$
2 ,, 3 ,, $0.399\ cos\ (t—235°.1)$
4 ,, 5 ,, $0.375\ cos\ (t—205°.4)$

The differences between these values are very small especially for the M_2-tide; for the O-tide the amplitudes show considerable fluctuations; but the agreement of the arguments clearly indicates that the differences between the experimental and theoretical values are due to an external periodical disturbance.

We shall presently see that they are caused by the watertides in the Indian Ocean and in the Java sea.

If, namely, we assume the amplitude of the undisturbed gravitation-tide M_2 to be equal to $^2/_3$ of its theoretical value — an assumption which cannot lead to an appreciable error considering the small value of this tide in proportion to the disturbing force — if, further, its argument is assumed to be equal to the theoretical argument, we find for the disturbing force:

$$0''\cdot00772\ cos\ (2t—2°.3)$$

If there were no retardation and, therefore, high water coincided with the moment of culmination of the fictive star, the tides would be represented for the longitude of Batavia by the expression:

$$R\ cos\ (2t—315.°5)$$

and the disturbance could be explained if the kappanumber of the ocean-tide is assumed to be:

North of Batavia $2°.3—315°.5 = 46°.8$
South ,, ,, $2°.3—315°.5 + 180° = 226°8.$

Applying the same reasoning to the O-tide (where, of course, the accuracy is less owing to the greater value of the amplitude if $^2/_3$ of its theoretical value is assumed) we find for the disturbing force:

$$0.''00765\ cos\ (t — 75.°7).$$

As, for kappa = 0, the watertide is:

$$R \cos (t - 312.°8)$$

the kappanumber ought to be:

North of Batavia 122.°9
South ,, ,, 302.°9.

Now the tidal constants according to VAN DER STOK [1]) are:

	Kappanumber	Amplitude in cm.
M_2-tide S. of Batavia	225°	49.6 [2])
,, ,, N. ,, ,,	304°	3.6 [3])
O ,, S. ,, ,,	268°	11.7 [4])
,, ,, N. ,, ,,	129°	9.3 [5])

If, as is reasonable, the principal disturbance of the M_2 tide is ascribed to the Indian Ocean, where semidiurnal tides are paramount, and, on the contrary, the disturbance of the O-tide is ascribed to the Java sea, where diurnal tides are prevalent, the agreement between the kappanumbers, as calulated from the disturbances and as observed, is very satisfactory.

A closer inquiry into the influence of the K_1 and P tides would be useless; the period of these tides being but slightly different from that of mean solar time, meteorological influences probably cause considerable disturbances: the results for different hours therefore show large discrepancies:

K_1 tide for 10 and 11^h $0.167 \cos (t - 315.°6)$
for 12 and 1^h $0.532 \cos (t - 224.°8)$
P tide for 10 and 11^h $0.187 \cos (t - 349.°7)$
for 12 and 1^h $0.538 \cos (t - 145.°3)$

Probably annual variations in the diurnal heat wave, and the intensity of land- and seawinds have an important disturbing influence [6]).

On the assumption that the disturbances acting upon the M_2 tide are wholly due to the watertide, the disturbance of the *E-W* component of this tide can be eliminated, as the disturbing force, acting on the *E-W* pendulum, in this case, has a difference of phase of about 90° and, consequently its influence on the amplitude is small.

If we look at VAN DER STOK's chart of homocumenes [7]), it appears that, south of Sumatra from Padang to Vlakkehoek, the kappanumber

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[1]) Kon. Nederl. Meteor. Instituut. Mededeelingen en Verhandelingen n°. 8. Elementaire theorie der getijden. Getijconstanten in den Indischen Archipel, 1910.

[2]) Amplitude at Tjilatjap, kappanumber according to chart of homocumenes.

[3]) ,, and kappanumber for Edam, Tandjong Priok and Duizendeilanden.

[4]) ,, ,, ,, for Tjilatjap.

[5]) ,, ,, ,, for Edam, Tandjong Priok and Duizendeilanden.

[6]) With sudden increase of the wind and the beginning of rainshowers, the direction of the wind can easily be traced on the seismograms; the deflections caused by these agencies amount to 1 à 2 mm. in maximo.

[7]) loc. cit.

(relative to Batavia time) is about 200°, whilst its average value in Sundastrait (Telok Betong, Java's 4th Point, Labuan) is 210°.

It is therefore reasonable to assume that over the whole region, where the disturbance exercised on the *E-W* pendulum originates, the kappanumber varies but slightly from 200°, say not more than 10°.

If we now calculate the disturbing force and the undisturbed earth-tide on the assumption that the kappanumber is 200° and that the argument of the undisturbed tidal motion of the ground is equal to its theoretical value, then we find [1]:

Amplitude disturbing force	0''.0026
,, corrected earth-tide	0''.0118

For the proportion between observed and theoretical amplitudes in the case of a rigid earth this gives the value 0.76.

Hecker also found for the *E-W* component the factor 0.76, and **Orloff** [2]) at Jurjew gives 0.63 as deduced by means of a **Zöllner** seismograph.

If we summarize the results given above, it is in the first place evident that great care must be taken in the choice of stations to be used for the determination of earth-tides, and that places situated in the vicinity of a sea with considerable tides are unsuitable for this purpose.

Further the unsatisfactory results obtained for the K_1 and P tides justify the conclusion that, in order to determine the constants of these tides, the instruments should be erected in a place sufficiently deep to eliminate tidal motions of meteorological origin.

It appears, further, that **Wiechert**'s pendulum is a very reliable and sensitive instrument, well suited for the determination of tidal motions and that, by means of its records, the diurnal as well as the semidiurnal tides may be determined without changing the erection usual for seismographic purposes.

If only the constants of the apparatus have been determined with sufficient care the material at present available from seismographs placed in favourable situations might at once be used for tidal researches without extra expense and the knowledge of the tidal problem might in this way be considerably extended.

For Batavia it proves to be possible to deduce the semidiurnal lunar tidal motion of the ground in the *E-W* direction notwithstanding the disturbance due to watertides.

Weltevreden, February 12, 1911.

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[1]) For kappa = 190° and 210° the amplitudes of the disturbing force are respectively 0''.0025 and 0''.0028, of the corrected tide 0''.0114 and 0''.0123.

[2]) Astronom. Nachr. No. 4446. Bd. 186.

Microbiology. — *"An experiment with Sarcina ventriculi"*. By Professor Dr. M. W. Beijerinck.

Some years ago I presented a paper concerning a method to obtain and cultivate an anaërobic fermentation *Sarcina* from garden soil. [1]) As the microscopic image and the dimensions of the thus obtained organism corresponded in all respects with the *Sarcina* of the stomach, [2]) of which Suringar [3]) has given so exact a description, I already then tried to prove their identity by experiments, similar to those with garden soil, with material containing stomach sarcina, which I owed to Professor van Leersum at Leiden. These experiments, however, failed. A later one, made at Leiden after my indications, proved likewise unsuccessful.

My supposition that the cause of the failure might have been a too strong aëration of the infection material by which the anaërobic stomach sarcina had lost all its vegetative power, induced me to pay special attention to this point at a renewed experiment for which Professor van Leersum again afforded me an opportunity in the Academic Hospital at Leiden.

It was proved that my supposition had been right: when transferring the contents of the stomach with the sarcina to a fit culture liquid, so quickly that contact with the air might be considered as excluded, it was possible to make the growth and fermentation proceed vigorously.

The experiment was managed as follows.

Some bottles of about 130 c.m.^{3} were filled with boiling malt extract quite freed from air by previous boiling. The malt extract was prepared by soaking about 20 g. of grist of kiln-dried malt in 80 g. of water, saccharifying one hour at 63° C., boiling and filtering. Some bottles were acidified with phosphoric acid to 5 cm^3 N per 100 cm^3, some others to 10 cm^3 N, and others were not acidified at all. The acidification was applied as the experience with the sarcina of the soil had taught that this organism endures a high

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[1]) Proceedings of the Meeting of 25 February 1905 p. 580. Archives Neérlandaises Sér. 2, T. 9. page 199, 1905.

[2]) Discovered by Goodsir, History of a case in which a fluid, periodically ejected from the stomach, contained vegetable organisms of an undescribed form. With a chemical analysis of the fluid by Wilson. Edinburgh Medical and Surgical Journal, T, 57, p. 430, 1842. Wilson asserts he has found acetic acid in the gastric juice, but does not speak of lactid acid, which is in fact produced by *Sarcina ventriculi.*

[3]) De Sarcine (*Sarcina ventriculi* Goodsir), Leeuwarden 1865.

degree of acidity much better than all other microbes occurring in the soil, so that the same might be expected with regard to the stomach sarcina if this were indeed identical with it. The further course of the experiment confirmed the correctness of this expectation too.

The bottles destined for the experiment were cooled after closing to about 40° C. and only opened at the moment the infection material was at hand, which consisted in the contents of the stomach of a person suffering of stenosis oesophagi. About 5 cm^3 of it was introduced into each bottle and that so quickly after the pumping out of the stomach, that the material had no time, neither to be saturated with air nor to be cooled considerably below the temperature of the body. Microscopically a great many sarcines were to be recognised, other microbes being hardly to be found. It is true that many yeast-cells occurred, but they proved dead and originated evidently from the yeast used for the preparation of the bread-porridge which the patient had eaten. Rests of potatoes and rice were also recognised in the contents.

Before proceeding the following observation may be mentioned here.

Directly after the pumping out of the stomach a little bottle was also quite filled with the thus obtained contents only, closed with a cork and placed in a thermostat at 37° C. The result was that in this bottle, already after a few minutes, so vigorous a fermentation set in that the cork was thrown off. As microscopic examination proved that in this way a very pure *Sarcina* fermentation was obtained, this simple experiment had for the first time demonstrated that the stomach *Sarcina* can be nothing else but an anaërobic fermentation sarcina.

The acid titer of the clear filtrate of the contents was, according to Professor VAN LEERSUM, 3.8 cm^3 N per 100 cm^3, with phenolphtalein as indicator, whilst free hydrochloric acid seemed quite absent, so that the acid must chiefly have been the lactic acid secreted by the sarcina itself, which is in fact very well possible, as at laboratory experiments the sarcina of the soil grows readily in somewhat saccharified meal-mashes and can form therein about 4 cm^3 N latic acid per 100 cm^3. The striking purity of the sarcina fermentation in so heterogeneous a mass as the stomach contents, in which neither lactic acid ferments nor alcohol yeasts were to be found, might have been explained by the presence of free hydrochloric acid, this acid being much better tolerated by the sarcina than by the other microbes. But as this acid seemed to be quite absent, the said pure development of the sarcina in the stomach, all other organisms being excluded, is not yet quite clear. But we return to our chief experiment.

The bottles prepared as described, arrived at Delft at a temperature of about 25° C. and were directly placed in a thermostat at 35° C. The result was that in all without exception, so as well in absence of acid as with 5 and 12 cm^3 N phosphoric acid, already after some hours a distinct fermentation was visible. By and by it increased in vigour and after about 18 hours the sarcina had so much multiplied, that at the bottom of the bottles a thick layer of the so characteristic microbe had deposited, from which an abundant current of fermentation gases, consisting of carbonic acid and hydrogen, mounted upwards. This state continued about 24 hours before the fermentation fell considerably.

My supposition that the earlier experiments had only failed because the stomach contents had been too strongly cooled and aërated during the transit from Leiden to Delft was thus proved to be well founded, and now all doubt is excluded about the identity of the soilsarcina of the hydrogen fermentations and the sarcina of the stomach.

It is of interest still to note here that in this experiment the addition of acid to the nutrient liquid had proved superfluous, as the fermentation had gone on also in the bottles without acid. In these latter bottles, however, many lactic-acid streptococci and lacto-bacilli were visible already after 18 hours' cultivation, which was not at all the case in the bottles with phosphoric acid. Only the latter could thus be used for the continuation of the fermentation by inoculation into a new quantity of culture liquid, without the chance that the sarcina might be overgrown and expelled by the lactic-acid ferments. Likewise as with the sarcina of the soil, by some repeated transfers into the described medium, acidified with phosphoric acid to 13 cm^3 N per 100 cm^3, it was possible within the course of three days to obtain so pure a culture of the sarcina, that inoculation into the malt extract without acid was successful, not any other microbes coming to development.

The thus obtained fermentations have become very vigorous and are not to be distinguished from the best fermentations with the soil sarcina.

Now that the identity of the latter and that of the stomach is ascertained, still the question exists how it feeds and multiplies at the low temperature and under the other conditions of life of the relatively cold soil, which must evidently be quite different as well from those of the stomach contents as from those of the described nutrient liquids, so rich in carbohydrates and various nitrogen compounds, and at temperatures between 35° and 40° C.

The answer to this question I hope to give later. That the sarcina should only accidentally occur in the soil and the mud of ditches and not multiply there, cannot be admitted on account of the very common occurrence of this organism; near the Laboratory at Delft, for example, the sarcina could easily be found to a depth of 70 cm in all earth-layers, even in so small quantities of soil as 0.1 to 0.5 g.

Why the sarcina develops so easily in the diseased stomach is in my opinion connected with the readiness with which this organism grows in meal-mashes, supported by the absence of hydrochloric acid which under normal circumstances inhibits all microbic growth in the stomach. The general occurrence of the sarcina is perhaps best shown by the following experiment. If some coarsely ground rye is mixed with water and placed in a thermostat at 30° to 35° C. it will the next day be found in a strong coli-aërogenes fermentation. If then this mass is carefully examined with the microscope many packets will be found of the sarcina in a state of very active multiplication. They clearly originate from the dust deposited on the surface of the corn at the reaping, the sarcina being quite well adapted to endure severe drying.

Although the sarcina of the stomach, in itself harmless, can at most be troublesome by the evolution of hydrogen, 1) it should still be observed that development of this microbe is impossible in absence of carbohydrates, so that at a flesh diet, if there were no reasons to avoid such a regimen, it would soon disappear. A milk diet, too, would have such a result, as well if the milk were acidified by lactic-acid ferments, as without previous acidification. So it was not possible in laboratory experiments to cultivate the sarcina in butter-milk, and even fresh milk, acidified with various quantities of lactic or phosphoric acid, gave only in few instances a feeble growth. In absence of acid the growth of the sarcina in crude milk is quite impossible, this organism being overgrown by the other microbes.

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1) The periodical vomitting observed in some cases of stomach sarcina may be connected with the accumulation of hydrogen, formed in the stomach.

Mathematics. — *"On the centra of the integral curves which satisfy differential equations of the first order and the first degree."* By Prof. W. KAPTEYN.

1. Considering x and y as the coordinates of a point in the plane, the real curves which satisfy a differential equation of the form $\frac{dy}{dx}=\frac{Q}{P}$, Q and P being polynomia in x and y with real coefficients, present different singularities. Between these we meet with points (foci) which are asymptotic points for the integral curves which present themselves as spirals in the neighbourhood of such points. These spirals sometimes change in closed curves and then the corresponding focus is called a centrum, and it is a question of great interest to determine the conditions when this happens. This question has been solved theoretically by POINCARÉ, but meets with great difficulties in practice.

The object of this paper now is to examine the differential equation, supposing P and Q to be polynomia of the second degree, and to determine all cases when centra may be expected instead of foci.

2. When the origin of coordinates is the point which must be examined, the differential equation may be written

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

where a, b, c, a', b', c', are real constants.

By substituting

$$\xi = hx + ky \qquad \eta = -kx + hy$$

the form of this equation is not changed, for we get

$$\frac{d\eta}{d\xi}=\frac{-\xi+\alpha'\xi^2+2\beta'\xi\eta+\gamma'\eta^2}{\eta+\alpha\xi^2+2\beta\xi\eta+\gamma\eta^2}$$

where

$$(h^2+k^2)^2\,\alpha = ah^3+(a'+2b)\,h^2k+(2b'+c)\,hk^2+c'k^3$$
$$(h^2+k^2)^2\,\beta = bh^3-(a-b'-c)\,h^2k-(a'+b-c')\,hk^2-b'k^3$$
$$(h^2+k^2)^2\,\gamma = ch^3-(2b-c')\,h^2k+(a-2b')\,hk^2+a'k^3$$
$$(h^2+k^2)^2\,\alpha' = a'h^3-(a-2b')\,h^2k-(2b-c')\,hk^2-ck^3$$
$$(h^2+k^2)^2\,\beta' = b'h^3-(a'+b-c')\,h^2k+(a-b'-c)\,hk^2-bk^3$$
$$(h^2+k^2)^2\,\gamma' = c'h^3-(2b'+c)\,h^2k+(a'+2b)\,hk^2-ak^3$$

Now h and k may be chosen so that the six coefficients $\alpha\,\beta\,\gamma$, $\alpha'\,\beta'\,\gamma'$ satisfy two conditions. Adopting

$$\alpha+\gamma=\lambda \qquad \alpha'+\gamma'=0$$

we have

$$(h^2 + k^2)\,\lambda = (a + c)\,h + (a' + c')\,k$$
$$0 = (a' + c')\,h - (a + c)\,k$$

so

$$h = \frac{a+c}{\lambda}\ ,\quad k = \frac{a'+c'}{\lambda}\ .\ .\ .\ .\ .\ .\ .\ .\ (1)$$

λ being a real number whatever, except zero.

From this it is evident that we may write

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

where still c could be replaced by $a - \lambda$. As we do not want this condition we will retain this coefficient in the old form.

Now after POINCARÉ's[1] theory here the origin is a centrum when it is possible to construct an infinity of homogeneous functions F_i of order i, satisfying the following series of partial differential equations

$$\left.\begin{aligned}
x\frac{\partial F_3}{\partial y} - y\frac{\partial F_3}{\partial x} &= 2xX + 2yY \\
x\frac{\partial F_4}{\partial y} - y\frac{\partial F_4}{\partial x} &= X\frac{\partial F_3}{\partial x} + Y\frac{\partial F_3}{\partial y} \\
x\frac{\partial F_5}{\partial y} - y\frac{\partial F_5}{\partial x} &= X\frac{\partial F_4}{\partial x} + Y\frac{\partial F_4}{\partial y}
\end{aligned}\right\}\ .\ .\ .\ .\ .\ (2)$$

. . . .

This leads to an infinity of conditions for the five constants a, b, c, a', b' and if these are all fulfilled the origin is a centrum and the general integral may be written

$$x^2 + y^2 + F_3 + F_4 + F_5 + \ldots = Const.$$

where the series converges until the closed curves, represented by this equation, pass through the nearest singular point.

3. The equations (2) may be transformed as follows. If we suppose F_n to be a homogeneous function of degree n, and $x\dfrac{\partial F_n}{\partial y} - y\dfrac{\partial F_n}{\partial x}$ to be divisible by $xX + yY$, the function $X\dfrac{\partial F_n}{\partial x} + Y\dfrac{\partial F_n}{\partial y}$ will also be divisible by $xX + yX$. For eliminating the differential quotients between

$$x\frac{\partial F_n}{\partial y} - y\frac{\partial F_n}{\partial x} = (xX + yY)\,P_{n-3}$$

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[1] Journ. de Math. (1885) p. 173.

$$Y\frac{\partial F_n}{\partial y} + X\frac{\partial F_n}{\partial x} = U$$

$$y\frac{\partial F_n}{\partial y} + x\frac{\partial F_n}{\partial x} = nF_n$$

we obtain

$$(xX + yY)(xY - yX)\,P_{n-3} - U(x^2 + y^2) + n(xX + yY)\,F_n = 0$$

which proves that U is divisible by $xX + yY$.

If therefore

$$U = (xX + yY)\,P_{n-2}$$

we have

$$(xY - yX)\,P_{n-3} - (x^2 + y^2)\,P_{n-2} + nF_n = 0 \quad . \quad . \quad . \quad (3)$$

and the conditions for a centrum may be written

$$x\frac{\partial F_3}{\partial x} - y\frac{\partial F_3}{\partial x} = 2\,(xX + yY)$$

$$x\frac{\partial F_4}{dy} - y\frac{\partial F_4}{\partial x} = X\frac{\partial F_3}{\partial x} + Y\frac{\partial F_3}{\partial y} = (xX + yY)\,P_1$$

$$x\frac{\partial F_5}{\partial y} - y\frac{\partial F_5}{\partial x} = X\frac{\partial F_4}{\partial x} + Y\frac{\partial F_4}{dy} = (xX + yY)\,P_2$$

. . . .

where evidently P_i represents a homogeneous function of order i.

These conditions may be further reduced, for

$$X\frac{\partial F_{n+2}}{\partial x} + Y\frac{\partial F_{n+2}}{\partial y} = (xX + yY)\,P_n$$

$$x\frac{\partial F_{n+2}}{\partial y} - y\frac{\partial F_{n+2}}{\partial x} = (xX + yY)\,P_{n-1}$$

give

$$\frac{\partial F_{n+2}}{\partial x} = xP_n - YP_{n-1}$$

$$\frac{\partial F_{n+2}}{\partial y} = XP_{n-1} + yP_n$$

hence

$$\frac{\partial}{\partial y}\left\{xP_n - YP_{n-1}\right\} = \frac{\partial}{\partial x}\left\{XP_{n-1} + yP_n\right\}$$

or

$$x\frac{\partial P_n}{\partial y} - y\frac{\partial P_n}{\partial x} = X\frac{\partial P_{n-1}}{\partial x} + Y\frac{\partial P_{n-1}}{\partial y} + \left(\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y}\right)P_{n-1}.$$

Remarking that $P_0 = 2$, the conditions (2) may finally be replaced by these

$$\left.\begin{aligned}
x\frac{\partial P_1}{\partial y} - y\frac{\partial P_1}{\partial x} &= \left(\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y}\right) P_0 \\
x\frac{\partial P_2}{\partial y} - y\frac{\partial P_2}{\partial x} &= X\frac{\partial P_1}{\partial x} + Y\frac{\partial P_1}{\partial y} + \left(\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y}\right) P_1 \\
x\frac{\partial P_3}{\partial y} - y\frac{\partial P_3}{\partial x} &= X\frac{\partial P_2}{\partial x} + Y\frac{\partial P_2}{\partial y} + \left(\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y}\right) P_2
\end{aligned}\right\} \quad . \quad . \quad (4)$$

etc.

4. Examining now the possibility of a series of homogeneous functions P_i satisfying the conditions (4), we introduce the values

$$X = ax^2 + 2b\,xy + cy^2 \qquad\qquad Y = a'x^2 + 2b'\,xy - a'y^2$$

$$\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y} = 2\,(a + b')\,x + 2\,(b - a')\,y.$$

Putting

$$P_1 = p'_0 x + p'_1 y$$

the first condition gives immediately

$$p'_0 = 4\,(a' - b) \qquad\qquad p'_1 = 4\,(a + b').$$

Thus the function P_1 divided by 4

$$P_1 = (a' - b)\,x + (a + b')\,y = p_0 x + p_1 y$$

always exists. Proceeding now to

$$P_2 = q_0 x^2 + q_1 xy + q_2 y^2$$

we find that this function exists when the coefficients satisfy the following equations

$$\begin{aligned}
q_1 &= (3a + 2b')\,p_0 + a'p_1 \\
2q_2 - 2q_0 &= (4b - 2a')\,p_0 + 2\,(a + 2b')\,p_1 \\
-\,q_1 &= cp_0 + (2b - 3a')\,p_1.
\end{aligned}$$

Therefore it is necessary that

$$(3a + 2b' + c)\,p_0 + 2\,(b - a')\,p_1 = 0$$

or that

$$(a' - b)\,(a + c) = 0.$$

By hypothesis $a + c \neq 0$, thus the first condition is

$$a' - b = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If this condition is fulfilled q_0 may be chosen arbitrarily, for instance $q_0 = 0$, and we have

$$P_2 = (a + b')\,[bxy + (a + 2b')\,y^2].$$

From this form it is evident that this function and all the following functions P_3 $P_4 \ldots$ vanish when

$$a + b' = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The origin is therefore a centrum if both the conditions (5) and (6) are satisfied.

In this case the integral of the differential equation

$$\frac{dy}{dx} = \frac{-x + bx^2 - 2axy - by^2}{y + ax^2 + 2bxy + cy^2}$$

takes the finite form

$$x^2 + y^2 + F_3 = const.$$

where F_3 may be determined from (3).

The integral curve

$$x^2 + y^2 - \frac{2}{3}bx^3 + 2ax^2y + 2bxy^2 + \frac{2}{3}cy^3 = const.$$

thus represents a series of closed curves round the origin of coordinates.

5. Assuming now

$$a' = b \text{ and } a + b' -= o$$

we may omit the factor $a + b'$ and write

$$P_2 = bxy + (a+2b')\,y^2 = q_1\,xy + q_2\,y^2.$$

Now it is always possible to find a homogeneous function

$$P_3 = r_0\,x^3 + r_1\,x^2y + r_2\,xy^2 + r_3\,y^3$$

satisfying the condition

$$x\frac{\partial P_3}{\partial y} - y\frac{\partial P_3}{\partial x} = X\frac{\partial P_2}{\partial x} + Y\frac{\partial P_2}{\partial y} + \left(\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y}\right)P_2$$

and the coefficients are found to be

$$r_0 = -\frac{b}{3}(a + 2c)$$

$$r_1 = b^2$$

$$r_2 = b\,(2a + 4b' - c)$$

$$r_3 = \frac{1}{3}(2a^2 + 10ab' + 3b^2 + 12b'^2).$$

Proceeding to

$$P_4 = s_0\,x^4 + s_1\,x^3\,y + s_2\,x^2\,y^2 + s_3\,xy^3 + s_4\,y^4$$

we find that the following relations between the coefficients of P_4 and P_3 must exist

$$s_1 = (5a+2b')\,r_0 + br_1$$

$$2s_2 - 4s_0 = 6br_0 + 4\,(a+b')\,r_1 + 2br_2$$

$$3s_3 - 3s_1 = 3cr_0 + 3br_1 + (3a+6b')\,r_2 + 3br_3$$

$$4s_4 - 2s_2 = 2cr_1 + (2a+8b')\,r_3$$

$$-s_3 = cr_2 - 3br_3$$

which are impossible unless

$$(5a+2b'+c)\,r_0 + 2br_1 + (a+2b'+c)\,r_2 - 2br_3 = 0$$

or

$$b\,(a+c)\,(2b' - 3a - 5c) = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

This condition breaks up into three conditions which will be considered separately.

Supposing in the first place

$$a' = b \text{ and } b = 0$$

the differential equation may be solved. For putting

$$\frac{x^2}{2} = t \qquad 1 - 2b'y = z$$

we obtain the linear differential equation

$$\frac{dt}{dz} - \frac{a}{b'z}\,t = \frac{1}{8b'^3} \cdot \frac{2b'+c - 2\,(b'+c)\,z + cz^2}{z}.$$

A particular integral of this equation being

$$t = \alpha + \beta z + \gamma z^2$$

where

$$\alpha = -\frac{2b'+c}{8ab'^2} \quad \beta = -\frac{2\,(b'+c)}{8b'^2\,(b'-a)} \quad \gamma = \frac{c}{8b'^2\,(2b'-a)}.$$

the general integral of the original differential equation takes the form

$$\{x^2 - 2\,(\alpha+\beta+\gamma) + 4b'\,(\beta+2\gamma)\,y - 8b'^2\,\gamma y^2\}\,(1-2b'y)^{-\frac{a}{b'}} = const.$$

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

$$x^2 + y^2 + F_3 + F_4 \ldots = const.$$

In this case therefore the origin is a centrum.

7. If, in the second place

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

the corresponding differential equation

$$\frac{dy}{dx} = \frac{-x + bx^2 + 2b'xy - by^2}{y + ax^2 + 2bxy - ay^2}$$

has three particular integrals of the form

$$y = Ax + B$$

for substituting this value and equalling the coefficients of the different powers of x in both members, we have

$$A\,(2bA - aA^2 + a) = 2b'A - bA^2 + b$$
$$A(2bB + A - 2aAB) = 2b'B - 2bAB - 1$$
$$AB\,(1 - aB) = - bB^2$$

which are satisfied by the roots of the cubic

$$aA^3 - 3bA^2 + (2b' - a)A + b = 0,$$

and by

$$B = \frac{A}{aA - b}.$$

In this case, the general integral may be written

$$(y - y_1)^{\lambda_1}(y - y_2)^{\lambda_2}(y - y_3)^{\lambda_3} = const.$$

where $y_1\ y_2\ y_3$ stand for the three particular integrals and $\lambda_1\ \lambda_2\ \lambda_3$ are certain constants. To prove this we will show that the necessary and sufficient condition [1]), that

$$(y - y_1)(y - y_2)(y - y_3)\left\{\frac{\lambda_1}{y - y_1} + \frac{\lambda_2}{y - y_2} + \frac{\lambda_3}{y - y_3}\right\}$$

is divisible by $y + ax^2 + 2bxy - ay^2$, may be fulfilled by choosing properly the constants $\lambda_1\ \lambda_2\ \lambda_3$.

This condition may be written, τ being a constant factor

$$\lambda_1 + \lambda_2 + \lambda_3 = - a\tau$$
$$\lambda_1(y_2 + y_3) + \lambda_2(y_1 + y_3) + \lambda_3(y_1 + y_2) = -(1 + 2bx)\tau$$
$$\lambda_1 y_2 y_3 + \lambda_2 y_1 y_3 + \lambda_3 y_1 y_2 = ax^2\tau$$

or, replacing $y_1\ y_2\ y_3$ by their values

(a) $\lambda_1 + \lambda_2 + \lambda_3 = - a\tau$

(b) $\lambda_1(A_2 + A_3) + \lambda_2(A_1 + A_3) + \lambda_3(A_1 + A_2) = - 2b\tau$

(c) $\lambda_1(B_2 + B_3) + \lambda_2(B_1 + B_3) + \lambda_3(B_1 + B_2) = - \tau$

(d) $\lambda_1 A_2 A_3 + \lambda_2 A_1 A_3 + \lambda_3 A_1 A_2 = a\tau$

(e) $\lambda_1(A_2 B_3 + A_3 B_2) + \lambda_2(A_1 B_3 + A_3 B_1) + \lambda_3(A_1 B_2 + A_2 B_1) = 0$

(f) $\lambda_1 B_2 B_3 + \lambda_2 B_1 B_3 + \lambda_3 B_1 B_2 = 0$

As

$$A_1 + A_2 + A_3 = \frac{3b}{a}\,,\quad A_1A_2 + A_1A_3 + A_2A_3 = \frac{2b' - a}{a}\,,\quad A_1A_2A_3 = -\frac{b}{a}$$

the conditions (a) (b) and (d) may be written

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[1]) KORKINE, Math. Ann. 48, p. 350.

$$\lambda_1 + \lambda_2 + \lambda_3 = a\tau$$
$$\lambda_1 A_1 + \lambda_2 A_2 + \lambda_3 A_3 = -b\tau$$
$$\lambda_1 A_2 A_3 + \lambda_2 A_1 A_3 + \lambda_3 A_1 A_2 = a\tau .$$

Hence

$$\lambda_1 = \frac{\tau}{N}(A_2 - A_3)(aA_1^2 - 2bA_1 - a)$$

$$\lambda_2 = \frac{\tau}{N}(A_3 - A_1)(aA_2^2 - 2bA_2 - a)$$

$$\lambda_3 = \frac{\tau}{N}(A_1 - A_2)(aA_3^2 - 2bA_3 - a)$$

where

$$N = A_1^2(A_3 - A_2) + A_2^2(A_1 - A_3) + A_3^2(A_1 - A_2)$$

and it is still to be proved that the three conditions (c) (e) and (f) are satisfied by these values of $\lambda_1\ \lambda_2\ \lambda_3$. Before proving this, we will write $\lambda_1\ \lambda_2\ \lambda_3$ in another form.

The values of $B_1\ B_2\ B_3$ expressed in the values $A_1\ A_2\ A_3$ are found to be

$$B_1 = \sigma(aA_1^2 - 2bA_1 - a)$$
$$B_2 = \sigma(aA_2^2 - 2bA_2 - a)$$
$$B_3 = \sigma(aA_3^2 - 2bA_3 - a)$$

and it is not difficult to find the value of σ. For introducing

$$A = \frac{bB}{aB - 1}$$

in the cubic, it is evident that the values of B are the roots of the cubic

$$2a(ab' - b^2)B^3 + (3b^2 - 4ab' - a^2)B^2 + 2(a + b')B - 1 = 0$$

Therefore

$$B_1 + B_2 + B_3 = -\frac{3b^2 - 4ab' - a^2}{2a(ab' - b^2)}$$

and

$$\sigma = \frac{1}{2(b^2 - ab')}.$$

Now

$$aA_1 - b)(aA_2 - b)(aA_3 - b) = N_1 N_2 N_3 =$$
$$= a^3 A_1 A_2 A_3 - a^2 b(A_1 A_2 + A_1 A_3 + A_2 A_3) + ab^2(A_1 + A_2 + A_3) - b^3 =$$
$$= 2b(b^2 - ab') = \frac{b}{\sigma}$$

and finally

$$\lambda_1 = \frac{\tau}{bN} A_1(A_2-A_3)N_2N_3$$

$$\lambda_2 = \frac{\tau}{bN} A_2(A_3-A_1)N_1N_3$$

$$\lambda_3 = \frac{\tau}{bN} A_3(A_1-A_2)N_1N_2.$$

With these values and $B_i = \frac{A_i}{N_i}$ the first member of (c) reduces to

$$\frac{\tau}{bN} A_1 (A_2-A_3)\,[2aA_2A_3 - b\,(A_2+A_3)] +$$

$$+ \frac{\tau}{bN} A_2 (A_3-A_1)\,[2aA_1A_3 - b\,(A_1+A_3)] +$$

$$+ \frac{\tau}{bN} A_3 (A_1-A_2)\,[2aA_1A_2 - b\,(A_1+A_2)] =$$

$$= -\frac{\tau}{N}[A_1\,(A_2^2-A_3^2) + A_2\,(A_3^2-A_1^2) + A_3\,(A_1^2-A_2^2)] = -\tau.$$

Further, the first member of (e) takes the form

$$\frac{\tau}{bN} A_1\,(A_2-A_3)\,A_2A_3\,[a\,(A_2+A_3) - 2b] +$$

$$+ \frac{\tau}{bN} A_2\,(A_3-A_1)\,A_1A_3\,[a\,(A_1+A_3) - 2b] +$$

$$+ \frac{\tau}{bN} A_3\,(A_1-A_2)\,A_1A_2\,[a\,(A_1+A_2) - 2b] = 0$$

and the first member of (f)

$$\frac{\tau}{bN}\{A_1A_2A_3\,(A_2-A_3) + A_1A_2A_3\,(A_3-A_1) + A_1A_2A_3\,(A_1-A_2)\} = 0.$$

The general integral is therefore

$$(y - A_1x - B_1)^{\lambda_1}\,(y - A_2x - B_2)^{\lambda_2}\,(y - A_3x - B_3)^{\lambda_3} = Const.$$

where

$$\lambda_1 : \lambda_2 : \lambda_3 = (A_2-A_3)\,(aA_1^2-2bA_1-a) :$$
$$(A_3-A_1)\,(aA_2^2-2bA_2-a) : (A_1-A_2)\,(aA_3^2-2bA_3-a).$$

When the cubic in A has a pair of imaginary roots the corresponding particular integrals are conjugate imaginary and therefore the general integral is imaginary unless two of the quantities λ are equal. This is only possible if $b(a+b') = 0$ and these cases have already been considered in Art. 6 and Art. 4. We must thus suppose that all the roots of the cubic in A are real.

For small values of x and y the general integral may be expanded in the form

$$x^2 + y^2 + F_3 + F_4 + \dots = Const.$$

which proves that in this case the origin is a centrum.

8. If we assume in the third place

$$a' = b \text{ and } 2b' = 3a + 5c$$

the corresponding differential equation takes the form

$$\frac{dy}{dx} = \frac{-x + bx^2 + (3a + 5c)\,xy - by^2}{y + ax^2 + 2bxy + cy^2} = \frac{-x + Y}{u + X}.$$

Here

$$\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y} = 5\,(a + c)\,x$$

and omitting constant factors we have, as before

$$P_0 = 2$$

$$P_1 = y$$

$$P_2 = bxy + (4a + 5c)\,y^2$$

$$P_3 = -\frac{b}{3}(a + 2c)\,x^3 + b^2x^2y + b\,(8a + 9c)\,xy^2 +$$

$$+ \frac{1}{3}(4a^2 + 115ac + 3b^2 + 75c^2)\,y^3.$$

$$P_4 = s_0x^4 + s_1x^3y + s_2x^2y^3 + s_3xy^3 + s_4y^4$$

where

$$s_0 = 0$$

$$s_1 = -\frac{b}{3}\,[8a^2 + 10ac - 3b^2 + 10c^2]$$

$$s_2 = 12b^2\,(a + c)$$

$$s_3 = b\,[44a^2 + 107ac + 3b^2 + 66c^2]$$

$$s_4 = \frac{1}{6}\,[308a^3 + 1245a^2c + 57ab^2 + 1675ac^2 + 69b^2c].$$

Proceeding to

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

and

$$P_6 = u_0x^6 + u_1x^5y + \dots + u_6y_6$$

we obtain

$$t_1 = (9a + 5c)s_0 + bs_1$$

$$2t_2 - 5t_0 = 8bs_0 + (11a + 10c)\,s_1 + 2bs_2$$

$$3t_3 - 4t_1 = 4cs_0 + 5bs_1 + (13a + 15c)\,s_2 + 3bs_3$$

$$4t_4 - 3t_2 = 3cs_1 + 2bs_2 + (15a + 20c)\,s_3 + 4bs_4$$

$$5t_5 - 2t_3 = 2cs_2 - bs_3 + (17a + 25a)\,s_4$$

$$-t_4 = cs_3 - 4bs_4$$

from which always the coefficients t may be determined, and

$$\begin{aligned} u_1 &= (10a + 5c)\, t_0 + bt_1 \\ 2u_2 - 6u_0 &= 10bt_0 + (12a + 10c)\, t_1 + 2bt_2 \\ 3u_3 - 5u_1 &= 5ct_0 + 7bt_1 + (14a + 15c)\, t_2 + 3bt_3 \\ 4u_4 - 4u_2 &= 4ct_1 + 4bt_2 + (16a + 20c)\, t_3 + 4bt_4 \\ 5u_5 - 3u_3 &= 3ct_2 + \;\, bt_3 + (18a + 25c)\, t_4 + 5bt_5 \\ 6u_6 - 2u_4 &= 2ct_3 - 2bt_4 + (20a + 30c)\, t_5 \\ -\; u_5 &= \;\, ct_4 - 5bt_5. \end{aligned}$$

From these the coefficients u may be found only when

$$(50a + 30c)t_0 + 12bt_1 + (14a + 18c)t_2 + 4bt_3 + (18a + 30c)t_4 - 20bt_5 = 0$$

or when

$$-\frac{20}{3} bt_1 + (10a + 6c)(2t_2 - 5t_0) + \frac{4}{3} b(3t_3 - 4t_1) +$$

$$+ \frac{1}{3}(34a + 30c)(4t_4 - 3t_2) + 4b(5t_5 - 2t_3) + \frac{1}{3}(190a + 210c)(-t_4) = 0.$$

Substituting now the values s, we have the condition

$$(a + c)\,[2bs_0 + (11a + 9c)\, s_1 + 6bs_2 + (17a + 27c)\, s_3 - 14bs_4] = 0$$

or

$$b\,(a + c)\,(ac + b^2 + 2c^2) = 0 \quad . \quad . \quad .. \quad . \quad . \quad . \qquad (8)$$

If $b = 0$, the differential equation reduces to

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

which has been considered in Art. 5.

If $a + c = 0$ we have

$$\frac{dy}{dx} = \frac{-x + bx^2 - 2axy - by^2}{y + ax^2 + 2bxy - ay^2}$$

which has been treated in Art. 7.

When however $ac = -b^2 - 2c^2$ the differential equation takes a new form

$$\frac{dy}{dx} = \frac{-cx + bcx^2 - (3b^2 + c^2)\, xy - bcy^2}{cy - (b^2 + 2c^2)\, x^2 + 2bc\, xy + c^2y^2}.$$

To solve this we will try to find particular integrals. If the conic

$$x^2 + 2Hxy + By^2 + 2Gy + 2Fy + C = 0$$

satisfies the equation,

$$-\frac{x + Hy + G}{Hx + By + F} = \frac{-cx + bcx^2 - (3b^2 + c^2)\, xy - bcy^2}{cy - (b^2 + 2c^2)\, x^2 + 2bc\, xy + c^2y^2}$$

must be equivalent with

$$(x^2 + 2H\,xy + By^2 + 2G\,x + 2F\,y + C)(\alpha x + \beta y) = 0.$$

This may be done by chosing $\alpha = -(b^2 + c^2)$, $\beta = 0$,

$$H = \frac{c}{b}, \quad B = \frac{c^2}{b^2}, \quad G = 0, \quad F = \frac{c}{b^2}, \quad C = \frac{c^2}{c^2(b^2+c^2)}.$$

Hence a first particular integral is the conic

$$(bx + cy)^2 + 2cy + \frac{c^2}{b^2+c^2} = 0.$$

In the same way we find that the differential equation is satisfied by the curve of the third degree

$$(bx + cy)^3 + 3cy\,(bx+cy) + 3cy + \frac{c^2}{b^2+c^2} = 0.$$

Combining these, the general integral is found to be

$$\left\{(bx+cy)^3 + 3cy\,(bx+cy) + 3cy + \frac{c^2}{b^2+c^2}\right\}^2 = Const.$$

$$\times \left\{(bx+cy)^2 + 2cy + \frac{c^2}{b^2+c^2}\right\}^3$$

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

$$x^2 + y^2 + F_3 + F_4 + \ldots = Const.$$

Therefore the origin is also a centrum in this case.

Resuming we may conclude that when the differential equation is reduced to the form

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

the origin is a centrum only in the four following cases

1. $a' = b$, and $a + b' = 0$
2. $a' = b = 0$
3. $a' = b$, $a+c = 0$ and the roots of
   $aA^3 - 3bA^2 + (2b'-a)A + b = 0$ all real.
4. $a' = b$, $2b' = 3a+5c$ and $ac+b^2+2c^2 = 0$.

In all other cases the origin will be a focus for the real integral curves.

Physics. — *"Some remarks on the value of the volumes of the coexisting phases of a simple substance."* I. By Prof. J. D. VAN DER WAALS).

The main features of the curve which represents the volumes of the coexisting phases as function of T, are known. It is a curve which possesses a maximum in the critical point for a volume which is equal to rb_g. The value of r would be equal to 3 for substances for which the quantity b is not variable. But for substances for which b does vary with the volume, r is smaller than 3. As this variability is greater, r will be smaller; it can be found by approximation from the relation $sr = 8$; or more accurately somewhat less than 8. In the critical point the liquid branch and the vapour branch meet. At this meeting the curve has a continuous course. Though this curve can only be experimentally determined at temperatures above the freezing point, there is every reason to consider these branches as also theoretically existing at lower temperatures. Even at temperatures above the freezing-point the liquid volume falls below the value of b_g. According to the determinations of SYDNEY YOUNG the coexisting liquid volume at 0° is e.g. for ether the $\frac{1,3583}{3,81}$ part of the critical volume, whereas the value of b_g cannot differ much from the $\frac{1}{2,1}$ part of v_k. And at lower temperatures this is regularly the case. On the vapour side the volume continually increases with decrease of the temperature on account of the great decrease of the pressure, and the relation $pv = RT$ is fulfilled more and more accurately. This holds both for anormal and for normal substances. Even for acetic acid, provided we bear in mind that the value of R for bi-acetic acid is meant, and do not consider acetic acid as an associating, but as a dissociating substance. But as long as the volume still has a finite value, there is still deviation from the law of the perfect gases, and SYDNEY YOUNG's observations (Proc. Royal Dublin Society. June 1910) present a valuable contribution to the discovery of the cause of this deviation.

That there will be a deviation, is of course to be expected according to the equation of state, even though we should leave quasi association entirely out of account. But the extent of the deviation could be accurately calculated in this case. Now the question can be answered if besides this cause of deviation there is another — and if we have to assume quasi-association to occur in such great volumes as those of the saturate vapours, and if this is sufficient to account for the differences found.

If we leave quasi-association out of account, the following equations would hold:

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

or

$$\frac{vp}{RT} = \frac{v}{v-b} - \frac{a}{vRT}$$

or

$$1 - \frac{vp}{RT} = \frac{a}{vRT} - \frac{b}{v-b} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

For the reduction to which I shall subject the second member of the equation (a) I refer to my "Quasi association" and to my paper in the Proceedings of the preceding month.

For the quantity $\frac{a}{vRT}$ I shall write $\frac{v}{v_k}\frac{a}{v_k RT_k}\frac{T_k}{T}$, or $\frac{v_k}{v}\frac{f_k-1}{s}\frac{T_k}{T}$; and though f_k cannot be determined absolutely accurately, and this is also the case with s, we yet know $\frac{f_k-1}{s}$ pretty accurately. If we write $\frac{T}{T_k} = m$, we find:

$$\frac{a}{vRT} = \frac{v_k}{v}\frac{f_k-1}{s}\frac{1}{m}.$$

In many cases SYDNEY YOUNG himself gives the value of $\frac{pv}{RT}$. In the last column of his numerous tables he gives namely the ratio of the real to the theoretical density of the saturate vapour. By theoretical density he understands that which would correspond to the formula $\frac{pv'}{RT} = 1$. Thus he gives for ether of 0° the value 1,028 for this ratio. So this means that for saturate vapour of ether at 0° the value of $\frac{pv}{RT}$ is equal to $\frac{1}{1{,}028}$. By substitution in equation (a) we have to investigate if:

$$1 - \frac{1}{1{,}028} = \frac{v_k}{v}\frac{f_k-1}{s}\frac{1}{m} - \frac{b}{v-b}.$$

Now it has appeared (see These Proceedings p. 1211) that even at the critical volume the deviation of b from b_g is only trifling. A fortiori this will be the case for great vapour volumes; and so we can write:

$$1-\frac{1}{1,028}=\frac{v_k}{v}\left\{\frac{f_k-1}{s}\frac{1}{m}-\frac{b_g}{v_k}\frac{v}{v-b_g}\right\}$$

or putting in the values v_k and v determined by SYDNEY YOUNG:

$$1-\frac{1}{1,028}=\frac{3,81}{1209}\left\{\frac{6}{3,813}\frac{466,8}{273}-\frac{1}{r}\frac{v}{v-b_g}\right\}.$$

Now that we are dealing with such great volumes, there is no objection to putting unity for $\frac{v}{v-b_g}$, and for ether r will not differ much from $\frac{8}{s}$, and so $\frac{1}{r}$ may be put equal to 0,48. The value of the first member is equal to 0,0273, and that of the second member to about 0,007. If such calculations are made at higher temperatures, e. g. for ether at 100°, we find for the value of the first member a greater number, viz. 0,172, and also for the second member a greater number, viz. 0,107. The difference, however, has become greater. Only at a much higher temperature this difference would again become smaller — but the ratio would always approach unity. At T_k the value of the first member is equal to $1-\frac{1}{s}$, and after some reduction the second member would also assume this value. And what has been said here for ether, holds almost unmodified for all substances examined by SYDNEY YOUNG, though there is some difference in the numerical values, which will be more fully discussed later on.

If we write the second member in the original form:

$$\frac{a}{vRT}-\frac{b}{v-b},$$

the thought might occur that by taking for a a function of the temperature which increases with decreasing value of T, the indicated difference might be removed. This, however, is only seeming, and this is one of the reasons why I have chosen the form $\frac{v_k}{v}\frac{f_k-1}{s}\frac{1}{m}$ for $\frac{a}{vRT}$. That this only seems to be so, and that we run a risk to make the difference still greater by putting such a function of T for a, may be demonstrated in the following way.

If we, namely, substitute $a\varphi\left(\frac{T_k}{T}\right)$ for a, we have:

$$p = \frac{RT}{v-b} - \frac{a\varphi\left(\frac{T_k}{T}\right)}{v^2}$$

$$T\frac{dp}{dT} = \frac{RT}{v-b} + \frac{a}{v^2}\varphi'\left(\frac{T_k}{T}\right)\frac{T_k}{T}$$

and

$$T\frac{dp}{dT} - p = \frac{a}{v^2}\left\{\varphi'\left(\frac{T_k}{T}\right)\frac{T_k}{T} + \varphi\left(\frac{T_k}{T}\right)\right\}$$

and

$$\frac{T}{p}\frac{dp}{dT} - 1 = \frac{a}{pv}\,\frac{\varphi\left(\frac{T_k}{T}\right) + \frac{T_k}{T}\varphi'\left(\frac{T_k}{T}\right)}{v}$$

So we have at T_k:

$$\frac{f_k-1}{s} = \frac{a}{v_k T_k R}\{\varphi + \varphi'\}_{kr}$$

For $\varphi\left(\frac{T_k}{T}\right) = \left(\frac{T_k}{T}\right)^{\mu}$ we write $\frac{a}{v\,RT_k} = \frac{f_k-1}{s}\,\frac{1}{1+\mu}$, hence

$$\frac{a\left(\frac{T_k}{T}\right)^{\mu}}{vRT} = \frac{v_k}{v}\,\frac{1}{m}\,\frac{f_k-1}{s}\,\frac{1}{1+\mu}\,\frac{1}{m^{\mu}}$$

If we compare this value with that which we obtained on the supposition of constant a, we see that it is

$$(1+\mu)\,m^{\mu}$$

times smaller. This expression can be either greater than 1 or smaller than 1. For $\mu = 1$ it becomes $2m$; and so for all values of m above $\frac{1}{2}$ the value which we had wished greater, becomes smaller on the contrary.

Nor could the supposition that b is a function of the temperature tend to make $\frac{a}{vRT}$ larger. In this case we should find:

$$\frac{a}{vRT} = \frac{v_k}{v}\left\{\frac{f_k-1}{s} - \frac{v_k}{(v_k-b_k)^2}\left(\frac{db}{dT}\right)_k\right\}\frac{1}{m}.$$

The explanation of this apparently paradoxical result must be found in this that if a had been a temperature function, $f_k - 1$ would also have been much greater, and we may accept this as an indirect proof that the quantity a is no function of the temperature.

So we have to look elsewhere for the cause of the fact that equation (a) does not hold, and to put the question whether the existence of quasi association can account for the found differences.

From the form for p, in the case of quasi-association, viz.:

$$p = \frac{RT}{v-b}\left\{1 - \frac{n-1}{n}x\right\} - \frac{a\left(1 - \frac{x}{2}\right)^2}{v^2}$$

we derive:

$$1 - \frac{pv}{RT} - \left(\frac{a}{vRT} - \frac{b}{v-b}\right) = x\left\{\frac{v}{v-b}\frac{n-1}{n} - \frac{a}{vRT}\left(1 - \frac{x}{4}\right)\right\}.$$

When applying this formula, when large vapour volumes are concerned we shall no doubt be allowed to put b equal to b_g, and neglect $\frac{x}{4}$ in the second member, and so we shall write this formula in the form

$$1 - \frac{pv}{RT} - \frac{v_k}{v}\left(\frac{f_k-1}{sm} - \frac{1}{r}\frac{v}{v-b_g}\right) = x\left\{\frac{v}{v-b_g}\frac{n-1}{n} - \frac{v_k}{v}\frac{(f_k-1)}{sm}\right\} \quad . \qquad (\beta)$$

So long as v is large compared with v_k we may, of course, put $\frac{v}{v-b_g} = 1$.

This equation (β) can serve to compute the value of x in the saturate vapour.

The value of the first member of (β) for ether has been given in the following table according to the mentioned observations.

0°	10°	20°	30°	40°	50°	60°
0,0203	0,0219	0,026	0,0335	0,037	0,0375	0,043

70°	80°	90°	100°	110°	120°
0,052	0,058	0,064	0,066	0,0675	0,07

130°	140°	150°	160°	170°	180°
0,071	0,07	0,062	0,057	0,045	0,016.

At T_k this difference, though it need not be equal to 0, must yet be a small fraction of x_k, as I have shown at the conclusion of my paper of the preceding month [1]. These calculated values cannot be considered as perfectly accurate; particularly on account of the uncertainty in the value of r and of f_k. This latter quantity I have put equal to 7. Probably the value 0,016 at 180° is too low.

The factor of x in equation (β) is the value of $-\frac{v\frac{dp}{dx_{vT}}}{RT}$, at least with a high degree of approximation. At very low temperature the

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[1] Proceedings of this meeting p. 1211.

limiting value is equal to $\frac{n-1}{n}$. With rise of T this quantity decreases. But we have concluded to such a value of n, $n > f$, that the factor of x is positive, even at T_k.

If we take $n = 9$, then $x = 0{,}023$ at 0° degrees, and x would rise at ascending temperatures, and assume the following values:

	100°	110°	120°	130°	140°	150°	160°	170°
x	0,088	0,095	0,103	0,113	0,12	0,122	0,13	0,136.

These values of x do not deviate too much from the formula:

$$\log_{10} \frac{x_k}{x} = 1{,}2 \frac{1-m}{m}$$

and then point to a value of $x_k = 0{,}16$.

But this relation cannot hold in the immediate neighbourhood of $m = 1$. Then the curve, which represents the course of x as function of m, would intersect the line $m = 1$ at an acute angle, whereas it must touch it. This follows also from the differential equation, according to which $\frac{T}{x}\frac{dx}{dT}$ depends on two terms, one of which is some times $\frac{T}{v}\frac{dv}{dT}$. As $\frac{T}{v}\frac{dv}{dT}$ is infinitely great at $T = T_k$, $\frac{T}{x}\frac{dx}{dT}$ will also be infinitely great. The factor of $\frac{T}{v}\frac{dv}{dT}$ is, however, small. So the curvature of the x-line will be less broad at the vapour side of the top — and $x_k = 0{,}16$ may be considered as an approximate value.

I have subjected other substances investigated by SYDNEY YOUNG to such an examination — and on the whole I have found a similar series of values for x with small differences in the course, which may later on yield material for investigation.

For normal pentane, which seems to have been investigated with particular care, as determinations have been made up to the immediate neighbourhood of T_k, I have represented the shape for x quite accurately, and tested it by the experimental determinations. The critical temperature is given equal to 197,2° and measurements have been made at:

196°, 196,5°, 196,8°, 197°, and 197,1°.

The accurate form for x is the following:

$$\frac{v}{v-b} - \frac{v_k}{v}\frac{(f-1)}{sm} - \frac{pv}{RT} = x \left\{ \frac{n-1}{n}\frac{v}{v-b} - \frac{v_k}{v}\frac{(f-1)}{sm}\left(1 - \frac{x}{4}\right) \right\}$$

The values of f I have taken equal to 7, that of $s = 3{,}766$, that of $b = 2{,}05$, and that of $n = 9$, and then we find for the value of the first member:

0,019, 0,023, 0,019, 0,01, 0,023.

We find for the factor of x:

0,193, 0,176, 0,146, 0,12, 0,129

and for x 0,1 0,13, 0,13, 0.083, 0,18.

If we consider how many numerical values which are not absolutely accurately known, have had to serve for the calculation, and how greatly an error in the measurements affects the slight amount of the expressions which determine x, the agreement must be called satisfactory.

I have undertaken this investigation: 1 to see if in the observations a support could be found for the existence of quasi-association, but chiefly 2 to try and find out what is the cause of the anormal behaviour of the alcohols. For this reason I have tried to determine the value of x for ethyl-alcohol.

The same reasons which made me conclude to the existence of quasi-association in general, apply also to alcohol. Very near T_k, e.g. at T only 0,6° different from $T_k = 516{,}1$, $\frac{T}{p}\frac{dp}{dT} - 1$ will not differ appreciably from $f_k - 1$, and $\frac{p}{p_k}$ exceedingly little from 1; hence it may be asked by way of simplication whether $\frac{v_1 v_2}{v_k^2}$ is found equal to $1 + (1-m)$ or equal to $1 + \sqrt{1-m}$. Now at

$$1 - m = \frac{0{,}6}{516{,}1} = 0{,}001164$$

we find the value of $\frac{v_1 v_1}{v_k^2} = 1.025$ for alcohol. Now 0,025 is certainly not equal to 0,001164, but of the order of $\sqrt{1-m} = 0{,}034$. We need only assume the value $v_k = 3.63$ given by SYDNEY YOUNG, to be equal to 3.61 to change the value 0,025 to 0.34. So we have every reason to expect for alcohol just as for the so-called normal substances, that a value for x will be found in the saturate vapour. I may mention here that long ago I concluded to the existence of molecule-complexes also for water vapour at 100°. Otherwise the volume which would be theoretically equal to 1689, would not have descended to 1649 — a diminution too great to be ascribed to the existence of a and b in the equation of state.

Proceeding in the above way, we find accordingly a value of x in the saturate vapour of alcohol, and in the value of x a course which does not deviate much from that which occurs for normal substances. Besides, also with regard to the relation I think I found in my paper of the preceding month between the critical quantities, viz. $\frac{s^2}{f-1}=\frac{64}{27}$, alcohol behaves in a normal manner. With $f_k=7,9$, to which value I concluded from SYDNEY YOUNG's observations we calculate $s=4,04$, while YOUNG gives 4,026 for it as determined by the observations.

If we apply the formula (γ) for the calculation of x, viz.:

$$\left(\frac{v}{v-b_g}-\frac{v_k}{v}\frac{f-1}{sm}-\frac{pv}{RT}\right)=x\left(\frac{n-1}{n}\frac{v}{v-b_g}-\frac{v_k}{v}\frac{f-1}{sm}\right)$$

we do indeed, meet with some irregularities for ethyl alcohol.

Thus for $\frac{pv}{RT}$ a same value equal to $\frac{1}{1.003}$ is given as well at 0° as at 10°, 20°, 30°, and 40°. For 0° $\frac{v_k}{v}=\frac{3.63}{30140}=0,00012$, which multiplied by $\frac{f-1}{sm}$ is equal to $1,714\times 1,89\times 0,00012=0,00039$, and which if we confine ourselves to thousandths, is too small to be taken into account. At 0° we should then find $x=\frac{n}{n-1}\,0,003$. At 40°, when $\frac{v_k}{v}$ has risen to $\frac{3.63}{3170}$, we should find x smaller and scarcely $\frac{n}{n-1}\,0,001$. But even if we should disregard this irregularity, it strikes us that at 40° x is evidently so much smaller for alcohol than it would be for ether in these circumstances and this suggests the thought that x descends more rapidly with the temperature for alcohol than it is the case for ether, or that perhaps it is smaller at all temperatures.

The latter seems hardly to be the case at higher temperatures.

Thus we find the value of the first member for alcohol at 130° equal to 0,044, whereas this value for ether for a volume that amounts to as many times the critical volume, which is the case between 60° and 70°, is equal to 0,05. At 190° the 1st member assumes a maximum value, which is equal to 0,067, which maximum value is only little greater for ether. And this maximum value occurs for both substances at volumes which are about an equal number of times the critical volume.

So our conclusion is that alcohol does not appreciably differ from the so-called normal substances as far as its saturate vapour volumes are concerned. But methyl-alcohol does behave in anormal way, both in the value of $\frac{s^2}{f-1}$, and in the value of $\frac{v_1 v_2}{v_k{}^2}$ near T_k. At a value of $1-m=0{,}0029$, and $\sqrt{1-m}=0{,}054$, $\frac{v_1 v_2}{v_{k_2}}$ is already equal to 1,14.

If also for methyl-alcohol for the saturate vapour we apply the formula:

$$\frac{v}{v-b_g}-\frac{v_k}{v}\frac{f-1}{sm}-\frac{pv}{RT}=-x\frac{v\left(\frac{dp}{dx}\right)_{vT}}{RT}\ .$$

and if we calculate the value of the first member from the data of Sydney Young, we find, indeed, the existence of a maximum value just as for all the other substances, but it lies much nearer T_k, and is much larger. Then we find for the value of the first member at the following series of temperatures:

0°	40°	120°	200°	210°	220°	225°	230°
0,009	0,028	0,072	0,094	0,124	0,154	0,126	0,119

The maximum occurs for $m=\frac{493}{513}$, while this occurs at $m=\frac{403}{466{,}8}$ for ether. Also in the volumes there is a great difference. For methyl-alcohol $\frac{v_k}{v}=\frac{3{,}674}{11{,}58}$, and for ether $\frac{3{,}63}{27{,}49}$. If this irregularity in the behaviour of methyl-alcohol is also to be ascribed to association, either quasi or real association, this substance yet agrees in so far with all the others that there is a value for $\left(\frac{dp}{dx}\right)_{vT}$, that it is even negative up to T_k, and that the positive value of $\frac{-v\left(\frac{dp}{dx}\right)_{vT}}{RT}$ decreases with the rise of temperature, and has even become exceedingly small at T_k. But x_k will be much greater than for the other substances.

But even though we should confine ourselves to normal substances the value of x_k appears to be much larger than I suspected when I wrote my "Quasi-association". It is true that I added there that I did not venture to assert that the values mentioned there would be correct. And immediately after the appearance of my paper I saw that all the numerical values mentioned there for x would require revision, which I have begun to do in this paper. Some of the values mentioned then would even give unstable phases, which I hope to prove later on. When judging about the value of x also in the saturate vapour, it must not be overlooked that when a molecule complex is considered as a compound molecule, the number of compound molecules amounts to the n^{th} part of this value of x. The number of simple and the number of compound molecules is then to each other as $1-x$ is to $\frac{x}{n}$.

In conclusion a remark on the value of $-\frac{T\,dv}{v\,dT}$ for the saturate vapour phases. Let us write $\frac{pv}{RT}=\varepsilon$, in which ε is the value obtained when unity is divided by the values from SYDNEY YOUNG's last table. At very low temperatures this value is only very little smaller than 1, e.g. for ether of 0° about $1-0{,}028$. With rise of temperature ε decreases, and for T_k it has descended to $\frac{1}{s}$. From $\frac{pv}{RT}=\varepsilon$ we derive:

$$\frac{T\,dp}{p\,dT}+\frac{T\,dv}{v\,dT}-1=\frac{T\,d\varepsilon}{\varepsilon\,dT}$$

from which follows:

$$\frac{T\,dv}{v\,dT}=\frac{T}{p}\frac{dp}{dT}-1-\frac{T}{\varepsilon}\frac{d\varepsilon}{dT}.$$

Now $\frac{T}{\varepsilon}\frac{d\varepsilon}{dT}$ is negative, and $-\frac{T}{\varepsilon}\frac{d\varepsilon}{dT}$ is exceedingly small for very low temperatures. At the zero-point of the temperature the value would be equal to 0, and even for $m=\frac{1}{2}$ it is still smaller than e.g. $\frac{1}{4}$. But it rises continually, and for T_k, for which $-\frac{T}{v}\frac{dv}{dT}$ is infinitely great, it will also have to be infinitely great. So there is also a temperature for which it is equal to 1. We can calculate from SYDNEY YOUNG's table at what temperature this takes place, and so at what temperature $-\frac{T}{v}\frac{dv}{dT}=\frac{T\,dp}{p\,dT}$. This temperature corresponds to $m=0{,}79$. For the different substances m varies only little. We shall discuss this temperature again, when we shall consider it as the temperature at which the product pv has maximum value.

So below this temperature the quantity $-\frac{T}{v}\frac{dv}{dT}$ is smaller than $\frac{T}{p}\frac{dp}{dT}$, but it is greater in the interval $m=0{,}78$ to $m=1$, rapidly increasing as it approaches to T_k.

Physics. — *"The lines H and K in the spectrum of the various parts of the solar disk".* By Prof. W. H. Julius.

§ 1. *Causes of line-shifts.*

There are at present four causes known, by which bright or dark lines of the solar spectrum may be displaced with respect to the position of the corresponding emission lines, as observed in laboratory experiments: radial motion, pressure, magnetic fields, anomalous dispersion. Which of these causes is likely to be the effective one, in each special case, can only be decided by comparing from a physical point of view the possibility of the conclusions to which the different suppositions lead us. If, e.g. we try to explain, by each of the four principles, the strong line-displacements often observed in the spectrum of prominences, it soon appears that both the second and the third principle are unable to give satisfactory solutions of the problem, so that, on further research, we shall only have to choose between the first and the fourth. On the other hand, the general displacement of the Fraunhofer lines toward the red, increasing from the centre to the limb of the solar disk, can be accounted for neither by Doppler's principle, nor by the Zeeman effect; so the interpretation of the phenomenon as a pressure effect has to be compared, in its consequences, with the interpretation on the basis of anomalous dispersion.

In a few cases there is scarcely any reason for doubt about the origin of certain line-displacements. Nobody will hesitate to ascribe the systematic differences between the spectra of the east and west limb of the sun to motion in the line of sight; nor question the magnetic origin of doublets and triplets in the spot-spectrum, which show the polarisation phenomena characteristic of the Zeeman effect. But such cases, where even at first sight only one explanation seems possible, are rare. It would be rash, e.g. to make magnetic forces at once responsible for the total widening of spot-lines, while other causes, that also produce widening, are known. As a rule, various influences co-operate; then the probably effectual cause of a solar phenomenon will only be brought out as such indirectly, by exclusion, that is, after other explanations have entangled one in ideas, clashing with general physical laws. And the remaining explanation will of course be the more probable, the better it joins some theory, already giving a coherent view of many other solar phenomena.

§ 2. *Phenomena exhibited by the calcium lines H and K.*

A remarkable case of systematic displacements, occurring with the calcium lines H and K, was first described by **Deslandres** in 1894, then by **Jewell** in 1896, and has recently been investigated very carefully on Mount Wilson by **Charles E. St. John**[1]), and at Meudon by **Deslandres**[2]). The main character of these phenomena is, that in the spectrum of the central parts of the solar disk the narrow dark lines H_3 and K_3 are displaced toward the red, the wider, bright lines H_2 and K_2 toward the violet; that these displacements decrease as we approach the limb, and that, on the other hand, the width of those lines increases from the centre to the limb. For further particulars we refer to the paper by **St. John.**

The peculiarities of the phenomenon cannot possibly be explained when pressure or magnetic forces are supposed to be the effective cause. **St. John**, who takes no notice of anomalous dispersion as a possible cause, is therefore so absolutely convinced of the radial-motion nature of the phenomenon (and so are **Deslandres** and **Jewell**), that he describes the results of his excellent observations under the title: "The general circulation of the mean- and high-level calcium vapor in the solar atmosphere".

We are going to show in the following pages, however, that all of the properties of the lines H and K, described by **Deslandres** and **St. John**, can be interpreted as consequences of anomalous dispersion. Thus, fortunately, one is *released from the necessity* of assuming, that in the solar atmosphere two opposite vertical currents of calcium vapour are continually kept up, meeting or perhaps passing or penetrating each other with velocities 30 or 60 times greater than the velocity of the most violent terrestrial blasts — and, marvellously, leaving the hydrogen and the other gases of the chromosphere unaffected! The explanation on the basis of anomalous dispersion does not involve such difficult physical notions, and offers the advantage, that it easily fits a theory, already connecting a great many other phenomena.

§ 3. *The influence of anomalous scattering on the distribution of light.*

The light coming from the lower strata of the sun, and having to traverse an extensive absorbing atmosphere, loses intensity not only by absorption, but also by *scattering.* It is true that radiant energy, when scattered, only alters its direction of propagation, not its nature (whereas, when absorbed, it suffers a change); so the scattered energy must finally quit the celestial body in the original form. But because part of it always returns to the source, we may

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[1]) **Charles E. St. John**, Astrophysical Journal, 32, 36—82, (1910).

[2]) H. **Deslandres**, C. R. 152, 233—239, (1911).

imagine that scattering *retards* radiation, and thus diminishes the output per unit time.

For kinds of light differing little in wave-length from the absorbed light, the coefficient of scattering is considerably greater than for light of the remaining parts of the spectrum, its value being proportional to the square of the refraction constant (according to RAYLEIGH), and the latter having great absolute values in the vicinity of absorption lines. Consequently the neighbourhood of the absorption lines must be more weakened by scattering, than the rest of the spectrum; which means, that the darkness of the Fraunhofer lines is partly due to anomalous dispersion.

How this conception of the solar spectrum follows from the theory of electrons, has been shown elsewhere[1]). We must now recall to mind some of the results there obtained.

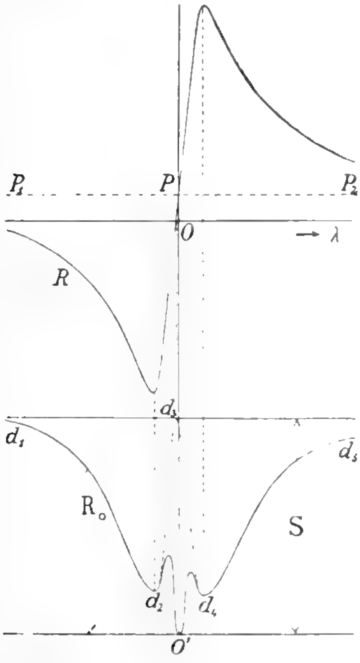

Fig. 1.

The curve representing the refraction-constant $R = \frac{n-1}{\Delta}$ as a function of λ, has in the region of an absorption line the shape, drawn in the upper part of fig. 1. On both sides of the line OP it approaches the almost horizontal line $P_1 P_2$, by which the course of the refraction constant of the medium would be represented if there were no absorption line at $O (\lambda = \lambda_0)$. If we compare with each other the absolute values of the ordinates of the curve R in points, situated at equal distances left and right of O, we find them always greater on the right side than on the left side. All effects, therefore, that increase with the absolute value of $n-1$, will manifest themselves more strongly on the red than on the violet side of the line. This applies 1st to the loss of light by scattering; 2nd to the intensity of the scattered light; 3rd to the rate of variety of brightness that may result from ray-curving, when there are density gradients in the medium. It follows, that on the average (i. e. apart from local irregularities) both the Fraunhofer

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[1]) W. H. JULIUS Selective absorption and anomalous scattering of light in extensive masses of gas. Proc. Roy. Acad. Amst. XIII, 881, (1911).

lines and the chromospheric lines are asymmetrical with regard to the exact positions of the emission lines, so as to have their "centres of gravity" somewhat displaced toward the red. One can easily show that this effect must increase from the centre toward the limb of the solar disk. Its character corresponds exactly to that of the systematic line-displacements, described in recent years by HALE and ADAMS, FABRY and BUISSON, and others, and considered by those investigators as consequences of pressure in the reversing layer. Objections to their interpretation, and arguments in favour of our explanation which is based on the shape of the dispersion curve, are to be found in former communications[1]). The part of the dispersion curve, lying between the minimum and the maximum, had not yet been taken into consideration then, that region being too narrow, with most Fraunhofer lines, to be observable by means of the spectral apparatus at present in use. But we are now extending our discussion to that middle part of the curve, which may perhaps reveal itself within a few very wide lines.

The lower part of fig. 1 (derived from the dispersion theory) shows, for the environment of a single absorption line, the intensity R_0 of the light transmitted by the solar atmosphere, if, for all waves considered, the intensity of the incident light is supposed to be S. The influence of *scattering* appears from the course of the (partly dotted) curve $d_1 d_2 d_3 d_4 d_5$; that of *absorption* from the shape of the additional part lying between d_2 and d_4, and showing a steep drop at O'. Only a few gases, strongly represented in the solar atmosphere, seem to exhibit so strong an absorbing power, that the minimum and the maximum of the dispersion curve are sufficiently distant from each other to make the phenomena, characteristic of the interval, perceptible.

Where this happens to be the case, we may expect to find, according to the dispersion theory[2]), that the "centre of gravity" of the central dark line is displaced toward the red, and that the apparent emission line, which is due to the scattering effect passing through a minimum at d_3, shows a displacement toward the violet. This simple deduction is in perfect agreement with the general phenomenon, observed by DESLANDRES, JEWELL, and ST. JOHN with the lines H_3 and K_3, H_2 and K_2, in the spectrum of the central parts of the solar disk.

§ 4. *The influence of anomalous refraction on the distribution of light.*

In order to find out how the effect will change as we approach

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[1]) Proc. Roy. Acad. Amst. XIII, p. 2, (1910); "Le Radium", VII, Oct. 1910.

[2]) Proc. Roy. Acad. Amst. XIII, p. 895, (1911).

the limb of the sun, we must fix our attention on another peculiarity of the propagation of light through matter. Indeed, anomalous dispersion implies not only anomalous *scattering*, but also, wherever the density of the medium is unequal, anomalous *refraction*.

Let us, for the present, leave out of consideration those "large-scale irregularities", characterized by more or less "systematically arranged" density gradients (such as probably exist in sun-spots)[1]), and imagine the average condition of the solar atmosphere to be like that of hot gases above a fire, i. e. a complex of irregular density gradients strongly varying from point to point in direction, magnitude, and sign. A very extensive layer of gas, thus constituted, must in some way act as a turbid or scattering medium. The optical effect produced by such an atmosphere will be comparable to what we observe when viewing a luminous surface through a plane-parallel glass tank in which, for instance, water and glycerine have just been stirred, but are not perfectly mixed yet. This "scattering by refraction" is, like molecular scattering, specially strong for kinds of light from the vicinity of absorption lines. So the effect of anomalous refraction is in many respects very similar to that of anomalous scattering, and will in so far only strengthen the latter.

But we should not overlook the difference between the two processes. The intensity of the effects of anomalous refraction depends on the degree in which there happens to exist *variety of density* in the medium. So it may be quite different at different places on the solar disk[2]), whereas the intensity of the effect of molecular scattering is more equally distributed, only increasing gradually from the centre to the limb. And, secondly, we must notice that the *direction* of the density gradients may strongly influence the intensity of the light emerging from the solar atmosphere along a given line. This circumstance too causes a kind of inequality in the distribution of the light, such as molecular scattering could not produce.

We are now prepared to inquire into the changes, which the distribution of the light in general, and the aspect of the calcium lines in particular, must show when we pass from the centre to the limb of the solar disk.

Those changes are of course closely connected with the fact, that in the central parts of the disk the main source of light has an almost symmetrical position behind the atmosphere, but not in the non-central parts.

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[1]) Proc. Roy. Acad. Amst. XII, p. 273, (1909).

[2]) The irregular distribution of the light in spectro-heliograms can be explained in this basis.

Fig. 2.

A point M somewhere in the atmosphere of the sun will be seen on the centre of the disk by an observer stationed on the line MA; but an observer on MB will see it not far from the limb. To the second observer the region round M appears much less bright than it does to the first one. This proves, that M receives less light (perhaps only half as much) along the direction bM than along aM. How, in a point M, the intensity of the irradiation by a definite kind of light depends on the direction of incidence, can easily be found, provided that we know the average distribution of the brightness on the solar disk, for the light in question.

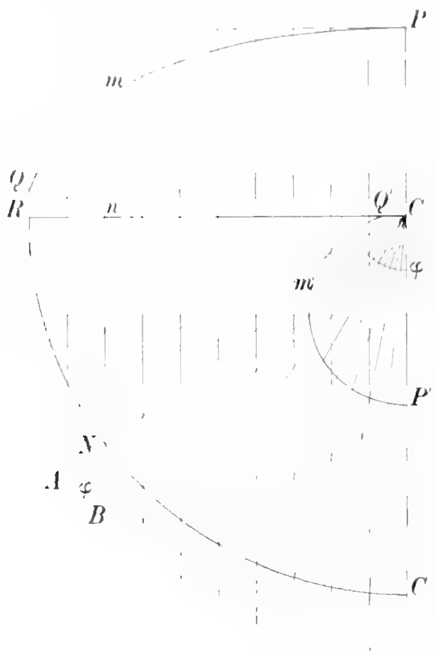

Fig. 3.

In fig. 3 PQ shows the gradual decrease of the brightness from the centre C toward the limb R of the solar disk for waves between 405 and 412 $\mu\mu$, according to spectro-photometric measurements by H. C. Vogel[1]). Let RNC' represent a section of the photospheric surface, and suppose an observer to be placed at a great distance in the direction CC'; then it is clear that e.g. from N — that is, in a direction making an angle ANB $(= NCC' = \varphi)$ with the normal to the photosphere, — an average quantity of light proportional to the ordinate mn of the $P'Q'$-curve, emerges from the solar atmosphere. We now define a point m' on the radius vector CN by making $Cm' = mn$, and do the same on the other radii of the section RNC'. Thus a curve $P'Q'$ is obtained, representing the transmissive power of the solar atmosphere for the selected kind of light, as a function of the angle of emergence φ. With the aid of this figure we may now proceed to the construction

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[1]) H. C. Vogel, Ber. der Berl. Akad., 1877, S. 104.

of the "irradiation-curve" for a point M (fig. 4) situated in the outer layer of the solar atmosphere. For that purpose we only have to take on each line MV, lying within the angle $H'MH$ and cutting the photosphere at an angle φ with the normal, a distance equal to that polar co-ordinate of the curve $P'Q'$ (fig. 3), which corresponds to the same value of φ. Joining the end-points of the vectors thus defined, we obtain the required irradiation curve qpq'. It differs only slightly in shape from $P'Q'$, and, as is easily seen, would preserve very nearly the same character if M were chosen in a lower level[1]).

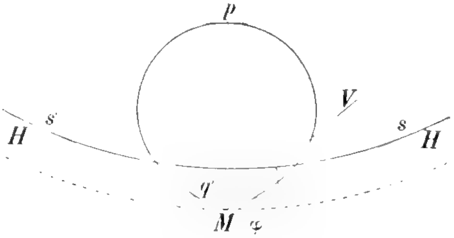

Fig. 4.

Now looking for an *explanation* of the general decrease of brightness toward the limb, it is only natural to make scattering responsible for the phenomenon (both molecular and refractional scattering). In fact, *all* kinds of light are more or less liable to scattering, whereas, very probably, absorption only extends to waves having the same, or almost the same frequency as the free vibrations of the electrons in the solar gases[2]).

The widening of the Fraunhofer lines toward the limb proves that the gradual decrease of intensity from centre to limb is greater for kinds of light suffering anomalous dispersion, than for the less refrangible light from blank spaces of the spectrum. Accordingly, if we construct the irradiation curve of a point M of the solar atmosphere for one of the strongly refrangible kinds of light from the vicinity of an absorption line, it will show a more oblong, oval shape than the curve that has been deduced, in fig. 4, from

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[1]) In this reasoning only the *observed* fact of the decrease of brightness toward the limb was taken for granted, no hypothesis regarding the cause of that phenomenon being required so far. The result, therefore, includes the full justification of the assumption on which our earlier considerations about the propagation of light through the solar atmosphere were based, viz. that the intensity of the light, incident on a small region M of that atmosphere, varies rather strongly with the direction (Proc. Roy. Acad. Amst. XII, 268, (1909)). Some astrophysicists objected to that view. Founding their refutation on the opinion, that a point of the solar atmosphere receives equal amounts of light (per unit of space-angle) from all directions meeting the photosphere, so that a circle $s'ps$ would represent the irradiation curve, they evidently left the above-mentioned elementary result of the observation of the sun entirely out of consideration.

[2]) Proc. Roy. Acad. Amst. XIII, 888, (1911).

VOGEL's observations on average violet light. This means, that for instance such waves as correspond to the places d_2 or d_4 of fig. 1, will reach a point M with an intensity that varies in a stronger measure with the direction in which they left the photosphere, than does the intensity of the average light.

Those very waves (near d_2 or d_4) are at the same time especially liable to *changing their direction of propagation* when there is a density gradient at M. If we were not concerned with anomalous *refraction,* but only with anomalous *scattering,* we should find that a definite kind of light would have a constant intensity, at any definite distance from the limb. But the refraction causes inequality. And the chance of observing a conspicuous variety of brightness, when looking at a region M of the solar atmosphere, which projects on the disk at a given distance from the limb, increases with the absolute value of $n-1$. By this circumstance we can e. g. explain a prominent feature of the spectroheliograms obtained by HALE and ELLERMAN [1]), viz. the gradual increase of the contrasts in a series of photographs of the same region, taken with waves, selected within K_1 at decreasing distances from K_3.

§ 5. *The co-operation of the two before-mentioned influences.*

The above discussion of the consequences of anomalous dispersion suggests the following interpretation of the variable, bright K_2-line, generally supposed to be an emission line.

There are two causes by which the brightness may increase on approaching K_3.

One of them depends on the presence of the two small (unequal) maxima of the R_0-curve in fig. 1, indicating a diminution of the loss of light by scattering. This influence acts almost equally in all points situated at equal distances from the centre; it is strongest on the middle parts of the disk; for in proportion as we approach the limb, the scattered light itself will contribute a greater share in the total emergent beam, thus levelling the curve and reducing the importance of the two small tops. The part of the effect, due to this first cause, is weak any how, even on the central parts of the disk, but of a constant nature: it always yields a narrow, double K_2-line, displaced toward the violet, and produces a displacement of K_3 toward the red.

The other cause depends on refraction in irregular density gradients. On the middle of the disk, refraction can only result in *diminution*

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[1]) Hale and ELLERMAN. The Rumford Spectroheliograph of the Yerkes Observatory. Publications of the Yerkes Observatory, Vol. III, Part I, 1903.

of the original brightness, and this effect must be strongest for the most refrangible waves corresponding to d_2 and d_4; K_2, which is situated there between those wave-lengths, is relatively narrow. But at some distance from the centre, where for every wave-length the average brightness is less than at the centre, density gradients may bring about, that light, emitted normally by the photosphere, curves toward the observer, thus producing a local increase of brightness.

Now again we fall back upon the most refrangible kinds of light, those at d_2 and d_4, as the ones that will be able to produce the latter effect in the strongest degree. Putting it otherwise: on the non-central places of the disk *refraction* will here and there contribute bright patches to the formation of the K_2-line, whose maxima of intensity have the greatest chance to correspond to the wave-lengths at d_2 and d_4. This effect combines with the before-mentioned scattering-effect. The components of K_2 must therefore, on an average, be farther apart than on the middle of the disk.

Proceeding toward the limb, the first part of the effect, that which is due to the dotted part of the scattering curve, diminishes, as already stated; while the second part, caused by refraction, gains in importance. Consequently the average distance between the components of K_2 increases, and, at the limb, becomes equal to that between d_2 and d_4. The bright components are not interrupted there by dark patches, as elsewhere on the disk, because at the limb the strongly *scattered* waves always enhance the brightness.

The influence of the two little tops of the R_0-curve, which on the middle of the disk determined the K_2-line, has disappeared near the limb; hence K_3 is wider than at the centre. Moreover, the displacements of K_3 and K_2 to the red and the violet respectively have gradually decreased on approaching the limb; for they depended on the asymmetry of the little tops. The points d_2 and d_4, determining the average places of the components of K_2 at the limb, are situated at equal distances from the real absorption line.

§ 6. *Weak points of the new and of the old explanation.*

While, all in all, these conclusions drawn from the dispersion theory show a very close agreement with the results of the observations, we should by no means neglect to pay due attention to the points where discordance exists or seems to exist. Only if searching for defects, one has a chance to improve one's views.

So we must notice that, if scattering and irregular refraction determine the phenomenon, we have some reason to expect asymmetry of K_2 near the limb; and if we were right in assuming the absolute value of $n-1$ to be greater at d_4 than at d_2, the red component should be a little stronger than the violet one. St. John, however, states [1]: "On the plates 1 mm. from the limb the emission components are very broad and strong, and, as far as the eye can judge, symmetrical". But on measuring the *width* of the components on some 30 selected plates, he found the violet one on the average 0,0074 Å wider than the red one. Surely the difference is small, but if it proves to be genuine, not accidental, our theory cannot, in its present form, explain the phenomenon — unless we are just here perhaps concerned with the case of asymmetry of the dispersion curve, treated of in § 3 of my former communication [2]).

Another case in which our theory perhaps falls short, is the following.

From published reproductions of spectrograms, obtained at Meudon and on Mount Wilson, I get the impression that the average distance between the brightest places of the K_2-components is greater at the limb than on very bright flocculi and faculae situated e.g. halfway between centre and limb. Now, according to our explanation, the position of the brightest patches of the components ought to be almost entirely determined by the position of the points d_2 and d_4, also in the spectrum of those brightest flocculi, because the part of the brightness which is due to the small intermediate tops of the R_0-curve is relatively slight in flocculi. That is: we should expect K_2 in the spectrum of very bright flocculi and faculae to be on the average not less wide than at the limb [3]). If the study of original plates confirms our suspicion that in this case the results of the observation contradict the theoretical conclusions, we shall have to correct the theory, or, if that is impossible, to reject it.

Finally attention must be called to some consequences resulting from the explanation given by Deslandres, Jewell and St. John of the phenomena exhibited by the H and K lines.

Among the greatest difficulties into which we are led by ascribing the line-displacements in question to ascending and descending currents, is in my opinion the one, already mentioned in the beginning of this paper: How is it possible, that in those violent vertical hurricanes of calcium vapour prevailing over the general surface of the sun, other gases of the chromosphere are not involved at all?

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[1] St. John. l. c. p. 54.

[2] Proc. Roy. Acad. Amsterdam, XIII, 885, (1911).

[3] In making the measurements, from which the gradual increase in width of K_2 and K_3 on approaching the limb has been deduced, St. John intentionally avoided the brilliant facular and floccular regions. Cf. l.c. p. 48 and 50.

Besides, the question arises, what can be the nature of the forces, giving such velocities to the co-existing rising and falling currents, and acting especially on *calcium*, not, or at least in a much lesser degree, on other gases? Some additional hypothesis is badly wanted here.

There are more difficulties, that one cannot avoid without introducing special hypotheses. The widening of K_2 towards the limb is explained by the continuous increase of the depth of the layer of radiating calcium vapour in the line of sight on approaching the limb. It is supposed that a sensible part of the beam of calcium-light, reaching the observer, has been able to travel a distance of 16000—62000 kilometers [1]) in a nearly straight line through a layer of the selectively absorbing solar gases, in which the average pressure is evaluated at one (terrestrial) atmosphere [2]). This conception seems to be opposed to the generally accepted theory of scattering and absorption of light. Moreover, one would expect, on the basis of the same explanation, to find the absolute brightness of K_2 increasing in passing from the centre to the limb. This, however, does not come true. Only in comparison with the neighbouring parts of the spectrum, K_2 increases in importance, but its absolute brightness decreases decidedly. In order to obtain spectrograms of nearly equal photographic density, St. John had to make the exposures 4 to 5 times longer at the limb than at the centre. The current explanation of the phenomena therefore requires the indication of an additional agent or process, by which the radiation of the chromosphere, although supposed to increase in passing from the centre to the limb, appears to decrease. One might e.g. assume the existence of a medium, surrounding the chromosphere in a rather thin layer, and having the property of absorbing all kinds of light in a certain degree

Similar additional hypotheses need not be introduced, if we explain the phenomena, exhibited by the calcium lines in the spectrum of the various parts of the solar disk, by means of the theory of the propagation of light through extensive masses of gas.

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[1]) St. John, l. c. p. 66.

[2]) St. John, l. c. p. 43.

Physics. — *"Further experiments with liquid helium. C. On the change of electric resistance of pure metals at very low temperatures etc. IV. The resistance of pure mercury at helium temperatures."* By Prof. H. Kamerlingh Onnes. Communication N°. 120^b from the Physical Laboratory at Leiden.

§ 1. *Introduction.* Since the appearance of the last Communication dealing with liquid helium temperatures (December 1910 liquid helium has been successfully transferred from the apparatus in which it was liquefied to another vessel connected with it, in which the measuring apparatus for the experiments could be immersed — in fact, to a *helium cryostat.* The arrangements adopted for this purpose which have been found to be quite reliable will be described in full detail in a subsequent Communication. In the meantime there is every reason for the publication of a preliminary note dealing only with the results of the first measurements made with this apparatus, in which I have once more obtained invaluable assistance from Dr. Dorsman and Mr. G. Holst. These results confirm and extend the conclusions drawn from the previous experiments upon the change with temperature of the resistance of metals. Moreover, it was, in the first place shown that liquid helium is an excellent insulator, a fact which had not hitherto been specifically established. This was of importance since the resistance measurements were made with naked wires, a method that is permissible only if the electrical conductivity of the liquid helium is inappreciable.

§ 2. *The resistance of gold at helium temperatures.* In the second place a link in the chain of reasoning which I adopted in § 3 of Communication N°. 119^B to show that the resistance of pure gold is already inappreciable at the boiling point of liquid helium has been put to the test by determining the resistance in liquid helium of the gold wire Au_{III}, which was then estimated by extrapolation on the analogy of the platinum-measurements. Within the limits of experimental error, which are indeed greater for the present experiment than was the case for the others, that value is now supported by direct measurement. The conclusion that the resistance of pure gold within the limits of accuracy experimentally obtainable vanishes at helium temperatures is hereby greatly strengthened.

§ 3. *The resistance of pure mercury.* The third most important determination was one of the resistance of mercury. In Communication N°. 119 a formula was deduced for the resistance of solid mercury; this formula was based upon the idea of resistance vibrators, and a suitable frequency ν was ascribed to the vibrators wich makes $\beta\nu = a = 30$ (β = PLANCK's number 4.864×10^{-11}). From this it was concluded:

1. That the resistance of pure mercury would be found to be much smaller at the boiling point of helium than at hydrogen temperatures, although its accurate quantitative determination would still be obtainable by experiment; 2. that the resistance at that stage would not yet be independent of the temperature, and 3. that at very low temperatures such as could be obtained by helium evaporating under reduced pressure the resistance would, within the limits of experimental accuracy, become zero.

Experiment has completely confirmed this forecast. While the resistance at 13°.9 K is still 0.034 times the resistance of solid mercury extrapolated to 0°C. at 4°.3 K, it is only 0.0013, while at 3° K it falls to less than 0.0001.

The fact, experimentally established, that a pure metal can be brought to such a condition that its electrical resistance becomes zero, or at least differs inappreciably from that value, is certainly of itself of the highest importance. The confirmation of my forecast[1]) of this behaviour affords strong support to the opinion to which I had been led that the resistance of pure metals (at least of platinum, gold, mercury, and such like) is a function of the PLANCK vibrators in a state of radiation equilibrium. (Such vibrators were applied by EINSTEIN to the theory of the specific heats of solid substances, and by NERNST to the specific heats of gases).

With regard to the value of the frequency of the resistance vibrators assumed before (one could try to obtain frequencies from resistances) it is certainly worth noting that the wave-length in vacuo which corresponds with the period of the mercury resistance vibrators is about 0.5 mm., while RUBENS has just found that a mercury lamp emits vibrations of very long wave-length of about 0.3 mm. In this way a connection is unexpectedly revealed between the change with the temperature of the electrical resistance of metals and their long wave emission.

The results just given for the resistance of mercury are, since they are founded upon a single experiment, communicated with all reserve.

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[1]) In connection with its deduction it is to be noted that the gold-silver thermo-element behaved in liquid helium quite so as the experiments in liquid hydrogen (KAMERLINGH ONNES and CLAY, Comm. N°. 107*b*) made expect.

While I hope to publish a more detailed description of the investigation which has led to these results in the near future, and while new experiments are being prepared, which will enable me to attain a greater degree of accuracy, it seemed to me desirable to indicate briefly the present position of the problem [1].

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[1] That this is justified is apparent from important papers which I have just received as this goes to press; in one NERNST extends the investigation referred to in Comm. N°. 119 of the specific heats and is also independently led to assume a connection between the energy of vibrators and electrical resistance, and in the other this hypothesis is further developed by LINDEMANN.

ERRATA.

In the Proceedings of the Meeting of March 25, 1911.

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