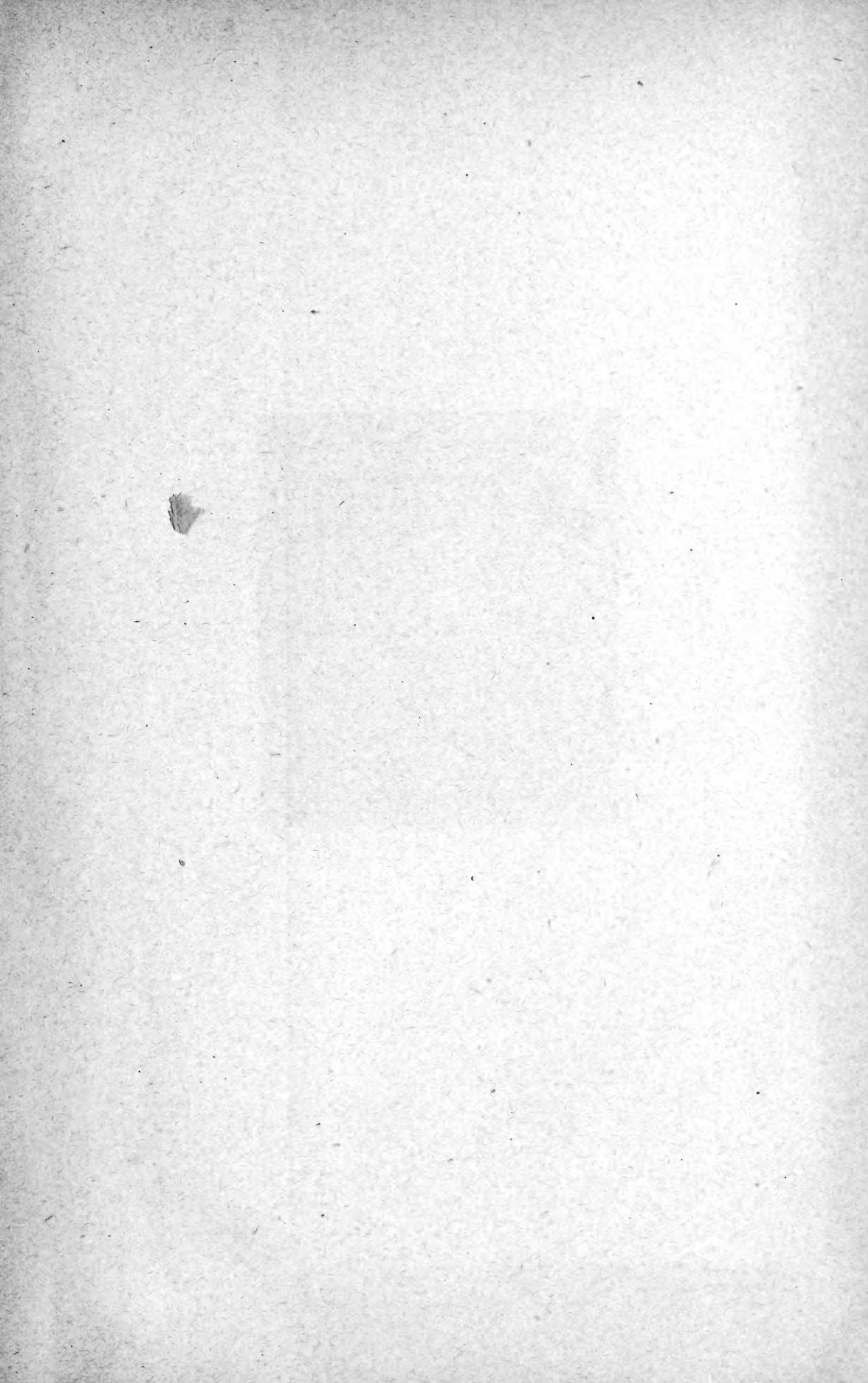
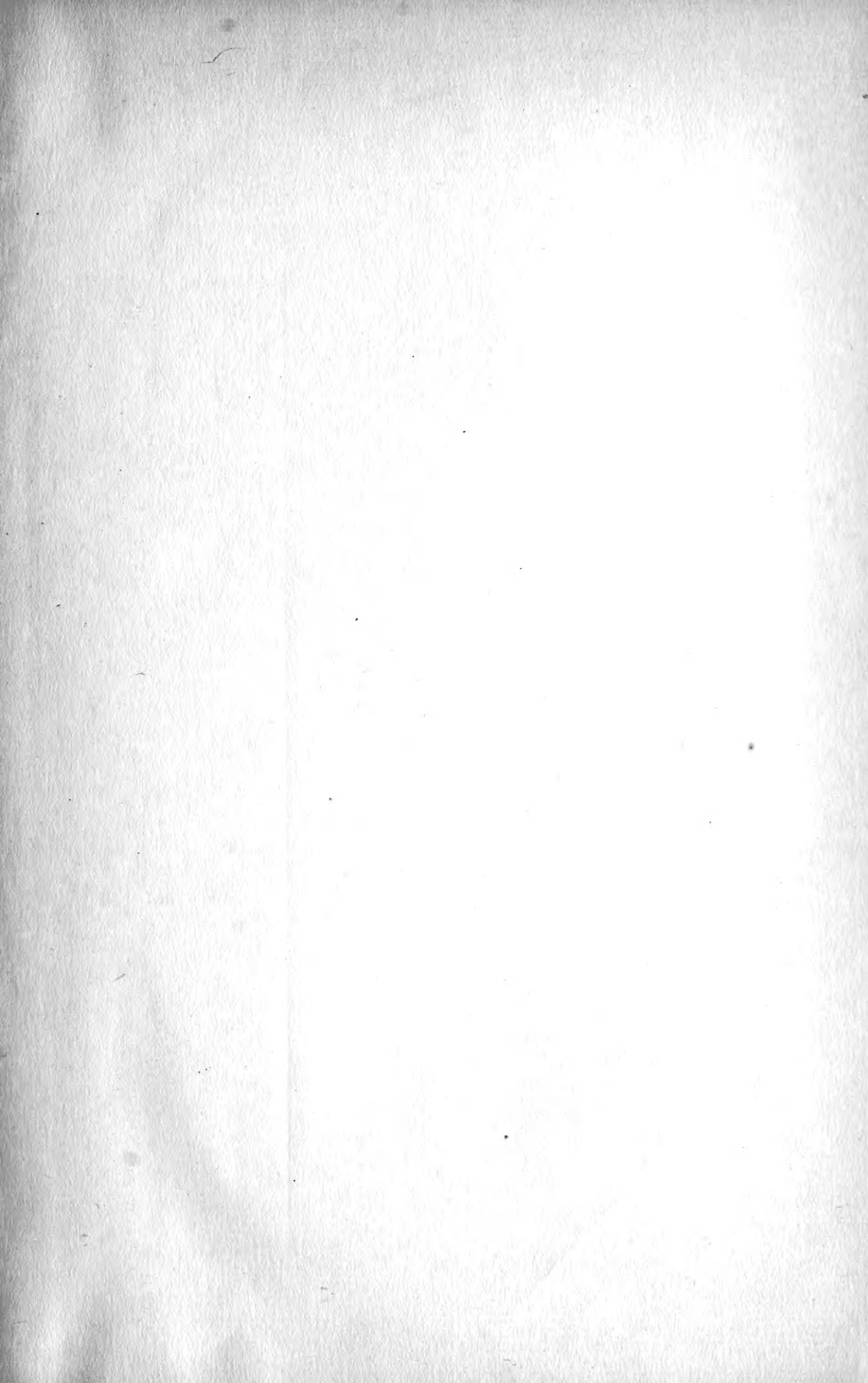


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PROCEEDINGS OF THE MEETING
of Saturday December 27, 1902.



(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige
Afdeling van Zaterdag 27 December 1902, Dl. XI).

C O N T E N T S.

- H. W. BAKHUIS ROOZEBOOM: "Tin amalgams", p. 373.
J. POTTER VAN LOON: "Benzidine transformation", (Communicated by Prof. C. A. LOBKY DE
BRUYN), p. 377.
K. F. WENCKEBACH: "On the duration of the compensatory pause after stimulation of the
auricle of the mammalian heart". (Communicated by Prof. C. A. PEKELHARING), p. 378.
J. CARDINAAL: "On the geometrical representation of the motion of variable systems", p. 386.
J. K. A. WERTHEIM SALOMONSON: "A new law concerning the relation between stimulus
and effect", (4th Communication). (Communicated by Prof. C. WINKLER), p. 392.
M. W. BELJERINCK and A. VAN DELDEN: "On a colourless bacterium, whose carbon food
comes from the atmosphere", p. 398.
L. H. SIERTSEMA: "The calculation $\frac{e}{m}$ from the magnetic rotation of the plane of polari-
sation, for substances without an absorptionband in the visible spectrum". (Communicated by
Prof. H. KAMERLINGH ONNES), p. 413.

The following papers were read:

Chemistry. — "*Tin amalgams*". By Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of November 29, 1902).

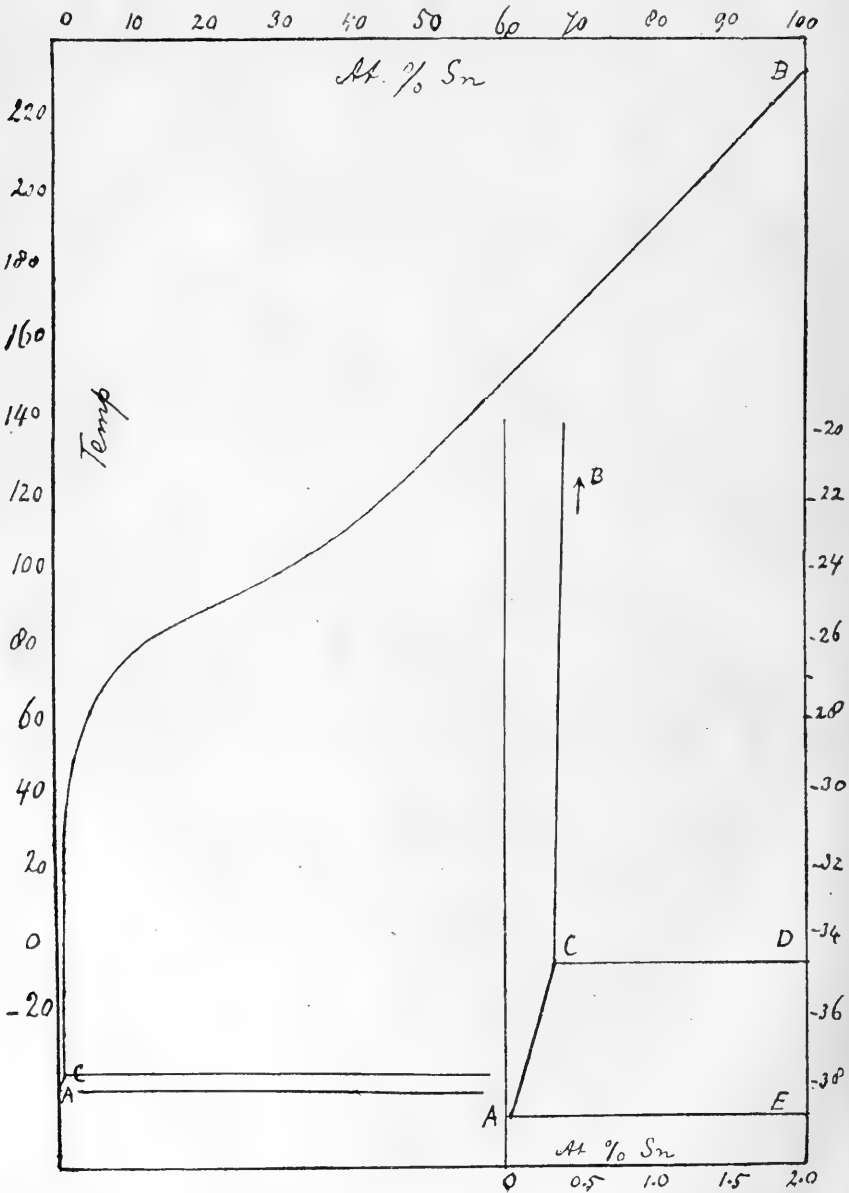
As the number of properly studied amalgams is still very small I directed Dr. VAN HETEREN to conduct an investigation on tin amalgams in connection with the research on cadmium amalgams by Dr. BIJL. The more important results are communicated here.

In the liquid condition tin and mercury are miscible in all proportions. From the different mixtures a solid phase is deposited at different temperatures. The points at which solidification begins are indicated in the accompanying figure by two lines *AC* and *CB*

which meet each other at *C* (0.3 at. % Sn and $-34^{\circ}.5$) in a sharp angle.

As the line *CB* ends in the melting point of tin, the solid phase which deposits on cooling must be either tin or mixed crystals in which ordinary tin occurs as a component. On analysis, the solid phase which has separated from the liquid amalgam at 25° was found to be composed of 94 atom % Sn.

On account of the difficulty of obtaining trustworthy results in



LINE BC.

At. % Sn.	Temp.	At. % Sn.	Temp.
100	231°.6	20.37	90°.0
89.95	244 .6	40.79	79 .7
76.62	483 .7	5.47	65 .2
61.44	455 .2	4.20	25 .0
49.99	433 .4	0.60	0 .0
35.33	407 .4	0.36	-18.8
28.96	99 .0	0.30	-34.5

this manner, measurements of the *E. M. F.* were also made at 25° of amalgams of 0.001—100 atom % Sn against an amalgam of 16 atom %.

These measurements led to the results that the unsaturated amalgams have a *E. M. F.* rising with the amount of tin until at 1.2 atom % saturation sets in. From this concentration up to 99 atom % the potential remains unchanged, consequently two phases of unchangeable concentration must exist between these limits; one of these is the liquid one of 1.2 %, the other the solid one containing 99 atom %.

At 25° the crystals deposited therefore consist of nearly pure tin which is the case in a still greater degree at higher temperatures. By a comparison of the values of the *E. M. F.* for amalgams of which the whole mass was liquid at 25° and 50° the heat of amalgamation could be calculated. The introduction of 1 gram-atom of Sn into a liquid amalgam with 0.01—1.00 atom % Sn, therefore nearly pure Hg, absorbs about 3000 calories.

The line *CB* may also be considered as the line of the solutions saturated with Sn. It takes a very peculiar course. The part from 120° up to the melting point of tin is nearly straight, the centre part shows a very rapid increase of the solubility with the temperature, the lower part, however, an exceedingly small increase and also an exceedingly small solubility so that the line approaches very closely the Hg-axis. In the lower part of the figure (p. 374) this part with its course towards the melting point of Hg has been drawn on a larger scale.

The extraordinarily great curvature of the central part of the line would lead to the supposition that the liquid mixtures of Sn + Hg in the absence of a solid phase would on further cooling separate into two layers.

On cooling below -34.5° a change takes place in all amalgams from 0.3 to 85%, accompanied by a decided evolution of heat and decrease of volume. With increasing concentrations of Sn it first increases but then decreases in intensity. The maximum lies near 50%. This change occurs in the figure on the line *CD* which therefore runs to at least 85%.

The change causes a new phase to appear which also belongs to the second solidifying-line *CA*. The maximum in the intensity of the change on *CD* at about 50% would lead us to suppose that mixed crystals having about this composition are formed. The modification of tin therein contained must differ from ordinary tin.

Between -34.5° and -38.5° these mixed crystals continue to be deposited from the mother-liquor (which moves along the line *CA*), this is accompanied by expansion. This change in volume diminishes as the amount of tin present increases and dies out near 75%. The solidification point of pure mercury and also the final solidification point of all amalgams containing up to about 60% Sn, lies at -38.6° (line *AE*). As the line *CA* of the saturated solutions also ends here it would seem that at the solidifying point of Hg, the solubility of tin has decreased to 0, so that instead of a eutectic mixture only the remaining mercury solidifies.

Still, the point *A* bears quite the characteristic of a eutectic point as not only the line *AE* is horizontal, but all mixtures up to 60% Sn also remain a shorter or longer time at this temperature which proves that a residual liquid is solidifying completely.

A great uncertainty still exists as to the nature of the tin-modification which occurs in mixed crystals below -34.5° chiefly because it has so far not been possible to discover the part played in the amalgams by the grey modification of tin which may occur below 20° C.

But from the change in volume which takes place in the different transformations at and below -34.5° we may argue that the specific volume of the tin must be smaller than that of the grey modification and larger than that of liquid and, therefore, also of ordinary tin.

Chemistry. — “*Benzidine transformation.*” By Dr. J. POTTER VAN LOON (Groningen). (Communicated by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the meeting of November 29, 1902).

It is known that hydrazobenzene when treated with a dilute mineral acid is converted into benzidine and diphenylene, benzidine being, however, the main product. I endeavoured to ascertain the proportion in which the isomers are formed and in how far this depends on the temperature and the concentration of the acid and I further attempted to measure the velocity with which the transformation takes place under definite circumstances.

Benzidine was obtained pure by recrystallisation from water and distillation in vacuo; the melting point of this substance was 128° which is in agreement with the statements of MERZ and STRASSER. (Journ. f. Pract. Ch. N. F. 60. 186).

For the preparation of hydrazobenzene, azobenzene was used as the starting point: this was purified by distillation and then reduced with zinc dust in an alcoholic alkaline solution. The hydrazobenzene so obtained was dissolved by warming in alcohol and the still yellow liquid decolorised by means of ammonia and zinc dust: the filtrate deposited pure white crystals of hydrazobenzene which could be separated unaltered from the liquid. A determination of the melting point gave as result 122°.

For the study of the transformation it was necessary to have a method for the quantitative determination of benzidine. It was found possible to do this gravimetrically by adding potassium sulphate to a solution containing not too much free acid and so precipitating the base as sulphate which was then collected on a weighed filter. According to my experiments, the slight solubility of benzidine sulphate amounts to 5—6 milligrams per 100 cc. of water at the ordinary temperature and consequently a correction should be applied. To ascertain in what proportion the two bases are formed during the transformation of hydrazobenzene, weighed quantities of this substance were put into bottles of about 120 cc. capacity and then shaken with a definite solution of an acid until all had dissolved. The benzidine present in the solution was then estimated, as directed, and the proportion calculated from the two data.

At the ordinary temperature, *N*/10 hydrochloric acid used in this manner causes 84 per cent of the hydrazobenzene to be converted into benzidine. Normal hydrochloric, hydrobromic acids convert 90

per cent of the same into benzidine. At a higher temperature the proportion is another, for in four experiments with one-tenth normal hydrochloric acid, nitric acid, sulphuric acid and hydrobromic acid the proportions at a 100° were respectively 66.4, 67.3, 63.1 and 65.8 per cent, therefore, much lower.

To get some data respecting the velocity of reaction a beaker with 50 per cent alcohol which contained hydrochloric acid in tenth-normal concentration was put into a thermostat and while stirring violently and passing a current of carbon dioxide over the surface a few grams of hydrazobenzene were introduced into the liquid in which that substance is but little soluble.

At 25°, the velocity appeared to be dependent on the concentration of the acid and it increased more rapidly than the concentration. The experiments are being continued in the two directions indicated above.

(Chem. Lab. Univers. *Groningen*).

Physiology. — “*On the duration of the compensatory pause after stimulation of the auricle of the mammalian heart.*” By Prof. K. F. WENCKEBACH. (Communicated by Prof. PEKELHARING).

(Communicated in the meeting of 29 November 1902).

When an extra-systole is set up by artificial stimulation of the ventricle or auricle of the beating frog's heart, this extra-systole is followed up by a pause longer than the pause succeeding a spontaneous systole. This long interval was studied by MAREY, DASTRE and others, and called a compensatory pause, because the longer quiescence of the heart was regarded as a compensation for the extra activity of the heart muscle. And it was not without reason that the word “compensation” was used, because the pause after an extra-systole is of such length, that the following spontaneous contraction just commences in the moment when it would have set in if, instead of an extra, a spontaneous systole had preceded. ENGELMANN (6) has given a simple and exhaustive explanation of the pause: the normal, physiological stimulus to contraction reaching the heart from the vena cava and causing it to contract finds, after an extra-systole auricle and ventricle in a refractory phase and so it cannot cause a contraction. It is only the following stimulus which finds the heart again in a condition in which it can react on that stimulus; the contraction (the “post compensatory”) then commencing, presents

itself precisely in the moment in which it would have commenced if the heart's action had been disturbed; so the rhythm of the physiological stimulation is not disturbed. In fig. 1¹⁾ the case is represented schematically. An artificial stimulus \uparrow reaches V . When the second stimulus arrives it finds the ventricle still refractory; so *one* systole is missing, but the following third stimulus, causes just at the right time again a normal systole. So the pause following the extra systole is with regard to its duration just compensatory; the time taken up by a spontaneous systole + extra systole and pause is just equal to that of two normal systoles.

If, however, we stimulate the frog's heart at the vena cava where the contraction always sets in, the compensatory pause is entirely missing and the following spontaneous systole succeeds the extra systole after a period equal to the normal period of contraction. In Fig. 1 the second artificial stimulus \Downarrow reaches the vena cava; the following spontaneous contraction sets in after the usual interval 20, a compensatory pause is missing. Whilst the interval between the systole preceding the extra systole and the one following the extra-systole after stimulation of the ventricle (or of the auricle) was double the normal period = 40, the same interval is here only $12 + 20 = 32$.

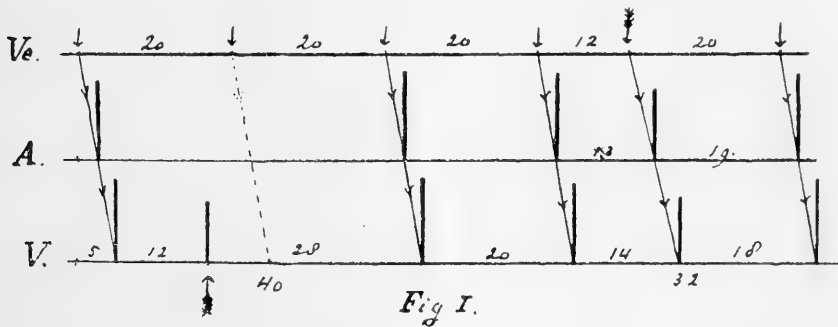


Fig 1.

From this ensues that the stimulus is not rhythmically induced from

¹⁾ In these schemes answering to those used formerly by ENGELMANN and by me the time is indicated on the three abscissae, and this is done for the duration of the phase and the stimulation of vena cava (V_e), auricle (A) and ventricle (V). \downarrow = physiological stimulus, \Downarrow = artificial stimulus. The perpendicular lines represent the contractions of the heart-cavities. The slanting lines connecting the base points of the systole-mark indicate the direction in which the stimulus is conducted. If these lines are dotted the conduction does not actually take place. The duration of the spontaneous period is put at 20 abscis units (= 1 mM.), the interval from the moment of the physiological stimulus to the ventricular contraction ($V_e - V_s$) = 5 units.

outside to the vena cava, but that it originates in that place in a definite period. It is certainly the most natural and the most suitable explanation of the phenomenon to assume that at the venae cavae (as is known to be the case in less degree in the other parts of the heart) continually stimulating matter is formed, till this obtains such a strength that a contraction is caused. When however, the muscle fibres contract the stimulating matter seems to have been used up or at least to have been destroyed, so that every time after a contraction the same time is wanted to produce new stimulating matter to such a strength that again a contraction follows. This destroying of the stimulating matter (dissociation in Ions, chemical changes or whatever this may be) always takes place when there is a contraction, whether the systole is caused by the stimulating matter itself or caused by a stimulus induced from elsewhere. For it is a well-known fact, that by artificial stimulation of the auricle or the ventricle, more frequent than the spontaneous rhythm, the latter can be entirely overpowered.

Another explanation is that at the vena cava there is a continual stimulation constant in strength, expressing itself periodically in systoles, because with each systole irritability, contractility and conductive power of the heart muscle are neutralized; so if a systole has taken place it always again lasts a certain time before the heart has recovered itself in so far that another contraction is possible. ENGELMANN objects to this, that the explosion brought about by the contraction in the molecular system of the muscle cell will destroy the stimulating matter in stock together with the other properties of this muscle cell, (irritability, contractility and conductive power); moreover did ENGELMANN show that the period of the formation of the stimulus can be changed independent of the irritability in the wall of the vena by chronotropic nerve influence. So we must assume that the systole destroys the stimulating matter and that every time the latter must again develop itself after every systole to active power. The law of the preservation of the physiological period of stimulation dominating the duration of the compensatory pause and all the important data come to light by means of "the method of the extra-systoles" for the frog's heart have been traced by CUSHNY and MATTHEWS (1) for the mammalian heart. These investigators showed that the mammalian heart obeys the same laws as the frog's heart, that its activity is dominated by the same fundamental properties of the fibres of the heart muscle, that the same theories hold good for both.

Only in one respect they found a difference: when the auricle is

artificially stimulated, the compensatory pause after the extra-systole is not as in the frog's heart truly compensatory but mostly of too short a duration. Sometimes it was completely compensatory, it was never entirely missing, it was generally shortened and then at any rate not equally shortened.

They say on this subject (l. c. page 226): „As long as the interval $A_s—A_p$ is of considerable length the compensatory pause in the auricle is truly compensatory, that is the interval between the last spontaneous contraction and the post-compensatory is equal to two auricular cycles. When however the stimulus falls earlier in the irritable period, no true compensation occurs, the post-compensatory contraction being premature, . . . when $A_s—A_p$ is short the compensation (of time W.) before the first natural contraction is always imperfect.”

The explanation of this difference is according to them: “either the contraction wave passes from the auricle to the great veins and there sets up a forced contraction which returning to the auricle causes the premature systole, or the irritability of the auricle gradually increases until it culminates in a contraction which is independent of the great veins and initiated in the auricular muscle itself. As to which of these two is the correct explanation we are unable to give any opinion and feel that it would be useless to balance probabilities before the movements of the great veins have been examined.”

Formerly I myself expressed the supposition, that the mammalian auricle might possess a greater automatic irritability, because in the phylogenetic development a part of sinus and vena would be taken up in the auricle.

H. E. HERING (2) has also been able to establish the difference described for the first time by CUSHNY and MATTHEWS; he says:

“The earlier the moment of stimulation falls in the irritable period of the auricle, the shorter the artificial bigeminus is (interval between last spontaneous and post-compensatory systole); the later it falls, the more the duration of the artificial bigeminus approaches that of two normal cardiac periods.” He continues: “the pause (after the extra-systole of the auricle) lasts longer according to the moment of stimulation falling earlier in the irritable period.” So here too he assumes the law of the conservation of the physiological period of stimulation: “aber die Beziehung ist keine so einfache wie am Ventrikel”.

We had all overlooked, that MACKENZIE (3) had become convinced already in 1894 after a careful analysis of the venous and liver pulse

that also in the human heart a "premature" contraction coming from the auricle is often succeeded by a too short compensatory pause. The possibility of distinguishing in this way between auricular and ventricular extra systoles had not escaped his attention.

When reflecting upon the consequences which extra systoles coming from the auricle must have on the action of the heart and the circulation of the blood of man, I found the following simple explanation of the above mentioned phenomenon, an explanation from which ensues that we have not got anything to do with a difference in principle between the frog's heart and the mammalian heart and that it is founded on an anatomic difference between the two hearts.

ENGELMANN (5) has shown that in muscular tissue of equal composition the stimulus to contraction is conducted also at an equal rate in all directions. So when an artificial stimulus is given to the auricle, a contraction stimulus and with it a contraction wave will pass from the stimulated point not only to the lower parts of the auricle and to the ventricle, but also to the higher parts of the auricle and to the vena cava, so to the place where normally the stimulus is formed and the contraction begins. ENGELMANN (6) has already pointed to the importance which this "antiperistaltic" movement may have for the action of the heart, CUSHNY and MATTHEWS have also seen the possibility of it.

When a stimulus is applied late in the irritable period of the auricle, so just before the moment when the following physiological stimulus was to come from the vena cava, the stimulus (and the contraction) will not be able to reach the vena cava any more before the physiological stimulus has had its effect there: auricle and ventricle will obey the extra stimulus, the spontaneous contraction already begun will not go on, but the rhythm at the venae is not disturbed.

If the extra-systole sets in a little earlier, the extra contraction might reach the vena cava just at the moment that the physiological stimulus had developed to the necessary intensity; then also auricle and ventricle obey the extra stimulus, the physiological stimulus is neutralized or it finds the whole heart refractory, but here too the rhythm of the formation of the stimulus is not disturbed and the pause of auricle and ventricle is completely compensatory.

When however the auricle is stimulated still earlier, the extra contraction will reach the vena cava before the moment, in which the stimulus to contraction forming there, had attained at sufficient strength to cause a contraction. The stimulating matter found there at that moment will be destroyed by the extra contraction: from this moment

new stimulating matter is being formed and after a certain time equal to the normal period it will have obtained enough intensity to cause another contraction. So the following spontaneous systole will *not* fall in the moment it would have done so if an extra systole had not been set up, but just so much *earlier* as the extra contraction reached the vena cava *before* the moment in which the following spontaneous contraction would have occurred.

In the diagrams II and III an attempt has been made at making these observations clear for a particular case.

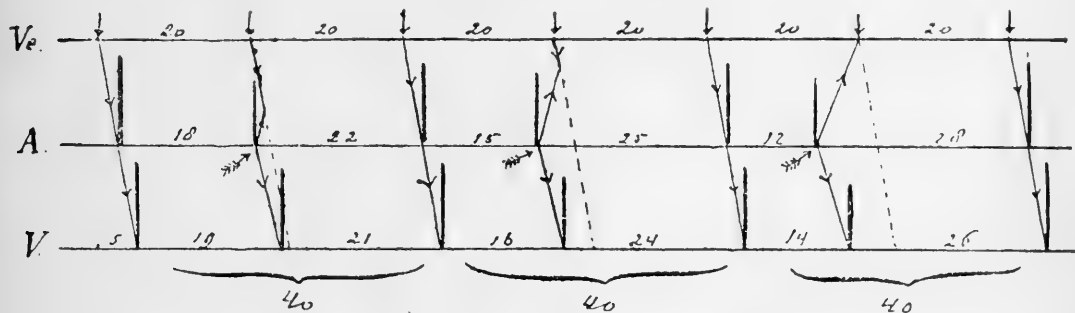


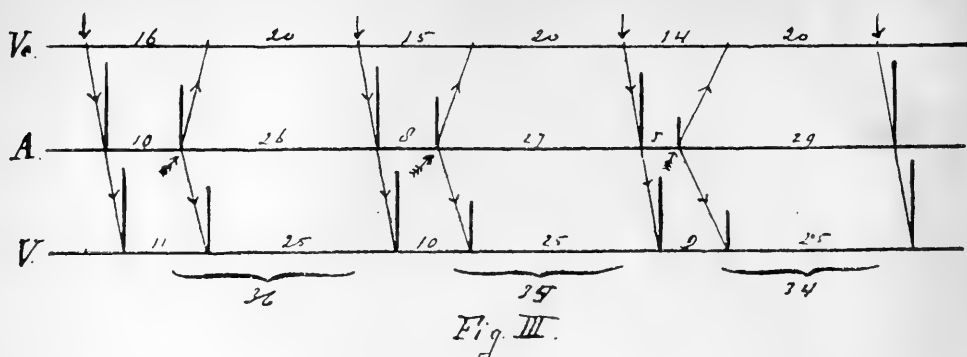
Fig. II.

In fig. II the auricle is artificially stimulated respectively 18, 15 and 12 units of time after the previous spontaneous contraction; auricle and ventricle follow the extra stimulus; in the first two cases the extra contraction moving to the vena cava intercepted the spontaneous contraction coming from the vena cava. In the third case it arrives in the vena cava just at the same time as the physiological stimulus becomes active. In all these cases the rhythm remains undisturbed and the compensatory pause is complete for the auricle as well as for the ventricle: the interval between the systole preceding the extra systole and the one following it is double the period of the heart, in this case = 40.

In fig. III an earlier stimulation of the heart is shown, 10, resp. 8 and 5 units of time after the preceding systole the auricle is stimulated. The extra systole formed by the first stimulus arrives in the vena cava 4 units *before* the following spontaneous contraction.

The stimulating matter present at that moment is destroyed and a certain time = 20 has to pass before the stimulus has increased to sufficient strength. So the interval of the spontaneous contractions is not = 40 but = $16 + 20 = 36$.

According to the extra auricular contraction falling earlier, this



interval must become shorter, a fact which goes without saying, in fig. III resp. = 35 and = 34.

From this ensues, that when the stimulation is effected late in the irritable period the compensatory pause is complete and furthermore, the earlier the stimulation is effected the shorter the interval between preceding systole and following spontaneous systole.

Another influence is still at work, which also governs the length of the pause. The earlier the stimulation is effected in the irritable period of the auricle, the slower the stimulus is conducted through the wall of the heart, for the conductive power of the cardiac muscle returns but gradually after the preceding systole. So the interval $A_s - V_{e_s}$ will be longer according to the stimulus being effected earlier and as this interval also dominates the moment in which the stimulating material is destroyed by the induced extra contraction it will also influence the length of the auricular interval. In fig. III where the slower conduction when the stimulus is effected earlier is taken into account this influence is illustrated. And in this way it is to be explained, that the interval is longer after an auricular extra-systole according to the moment of stimulation falling earlier in the irritable period of the auricle following quicker upon the preceding systole.

The differences in length of the compensatory pause after stimulation of the auricle are in this way easily explained and it appears that the rules established for the amphibian heart hold good for the mammalian heart, in the sense however, as HERING says, that "die Beziehung keine so einfache ist".

The peculiar modifications in the course of the extra contraction when the auricle is stimulated, derived by MACKENZIE from the venous pulse, by CUSHNY and MATTHEWS from the tracings of the auricular movements, will probably find their explanation in the way in which, as is proved in fig. II, the contraction waves meet here in the auricular

wall and the differences will depend upon the spontaneous or the extra contraction being the most considerable.

The question must however now be put: why does a complete compensatory pause always (or almost always, ENGELMANN ⁶) follow the extra systole of the auricle in the amphibian heart and why in the mammalian heart only under certain conditions?

The answer may run as follows: In equally built up parts of the heart muscle the stimulus is also equally conducted to all sides, but where for whatever reason the state of the muscle fibres is not everywhere the same, the conduction of the stimulus will neither be the same. This is the reason that the conduction of the stimulus of the auricle on the ventricle, in general of one division of the heart on the other, takes place much slower than inside the wall of auricle or ventricle. When conduction takes place in the direction opposed to the normal, this distinction will not make itself less felt. And just as the slower conduction may be the cause that extra-systoles of the ventricle never recede quickly enough to have a disturbing effect on the rhythm of the great veins, the differentiation between veins, sinus and ventricle in the frog's heart will be the cause, that here a stimulation of the auricle is not quickly enough conducted through the transition places to disturb the rhythm at the venae cavae. Moreover this possibility seems so much the slighter, because in the frog's heart muscle fibres with a strong automatic irritability ascend high up in the vena cava and so cannot be reached so easily by an extra stimulus. As this differentiation of the cardiac muscle between vena cava and atrio-ventricular limit is missing for the mammals, it is no wonder that the disturbing influence on the formation of the stimulus at the vena cava occurs just in the mammalian heart.

If finally this explanation is the right one, the place where the auricle of the mammalian hearth is stimulated, will have its effect on the length of the compensatory pause: perhaps it will be possible to establish for not too small hearts and where the conduction of the muscle has already somewhat slackened, that for auricular stimulation far from the vena cava the compensatory pause is longer or even complete, whilst the pause becomes shorter according to the auricular stimulation taking place closer to the vena cava. For such an experiment the stimulation would always have to be effected exactly in the same moment of the heart period, every time equally long after the preceding systole.

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Mathematics. — "*On the geometrical representation of the motion of variable systems*". By Prof. J. CARDINAAL.

1. In two communications ¹⁾ some theorems have been developed by me, relating to the motion of variable systems. Also in this subdivision of the doctrine of motion the method of the geometrical representation occurring so frequently in Mathematics can be applied. The following communication has in view to mention some particulars on this subject. The representation in question is treated ²⁾ by R. STURM. From this treatise I derive the short summary, which must needs appear here as an introduction to the subject.

2. In the quoted considerations two complexes of rays played an important part, namely the tetrahedral complex formed by the directions of the velocities of the points of the moving system and the rays of a focal system belonging to it; the latter consists for the motion of an invariable system of the normals of the trajectories of the points and for a projectively variable system of rays whose construction took a great part of the considerations. The purpose must be to obtain a simultaneous representation of complex and focal system; it will prove desirable to give the foremost place to the representation of the focal system.

3. Let thus be given the focal system \mathcal{A} situated in the space Σ . According to the method of SYLVESTER let us suppose two planes ξ and ζ with two projective pencils of rays situated in them with their vertices N' and N situated on the line of intersection $\xi\xi' \equiv \zeta\zeta' \equiv e$,

¹⁾ Proceedings of the Kon. Akad. van Wetensch., section of science, vol. IV, pages 489 and 588.

²⁾ Die Gebilde ersten und zweiten Grades der Liniengeometrie, I, p. 257.

x being an homologous ray of both pencils. The rays of \mathcal{A} are the transversals of two homologous rays of $(X\xi')$ and $(X'\xi)$.

Let us now take two sheaves of rays in the space Σ_1 with the vertices X_1 and X'_1 and establish a projective correspondence between these sheaves and the pointfields ξ and ξ' , in such a way that the pencil of planes through the axis $X_1X'_1$ is homologous to the pencils $(X\xi')$ and $(X'\xi)$. Let l be a ray of \mathcal{A} , cutting two homologous rays of $(X\xi')$ and $(X'\xi)$, to which in the homologous plane λ_1 a ray l_1 out of X_1 and a ray l'_1 out of X'_1 correspond; l_1 and l'_1 intersect each other in a point L_1 . This point is homologous to the ray l . So a projective correspondence is established between the points of the space Σ_1 and the rays of the focal system \mathcal{A} .

As is the case with every representation, also here the knowledge of its principal curve cannot be dispensed with. It is a conic X_1^2 through the points X_1 and X'_1 situated in a plane ξ_1 . Its points are homologous to the pencils of rays of \mathcal{A} situated in planes through x . The plane ξ_1 (principal plane) itself is homologous to x .

To an arbitrary pencil of rays of \mathcal{A} a right line corresponds cutting X_1^2 , to a hyperboloidic system of focal rays a conic having two points in common with X_1^2 , to a linear congruence belonging to \mathcal{A} a quadratic surface through X_1^2 .

4. Let a projectively variable moving spacial system be given; let as before $PQRS$ be the tetrahedron of coincidence of two successive positions and let the corresponding focal system \mathcal{A} be determined by PQ and RS as conjugate polars and the conic K^2 touching PR and PS in R and S . According to the indicated method the focal system can be represented in the space Σ_1 ; for the tetrahedral complex of the directions of the velocities, however, we need another representation, which can be taken in such a way that the same principal curve is retained; we shall succeed in this if we do not represent the complex itself, but its section with the focal system \mathcal{A} . This gives rise to a congruence (2,2) which we shall first investigate more closely.

5. Let \mathcal{A} be an arbitrary point, α its focal plane; at the same time \mathcal{A} is the vertex of a quadratic cone, geometrical locus of the directions of the velocities through \mathcal{A} , but of which only one is the direction of velocity of \mathcal{A} itself. This cone will cut in general α into two rays belonging to the congruence (2,2); in this way we can construct the whole congruence. By this we have determined the construction, but not the geometrical character of the congruence; this can be done in the following manner:

Let the direction of the velocity a of a point A intersect the plane of coincidence PRS in L ; now the focal plane of A intersects this plane in the polar p of L with respect to the conic K^2 . The rays of the complex, at the same time rays of the conjugate focal system, are situated in the focal plane α of A ; from this ensues that these rays intersect the plane PRS in two coincident points, at the same time conjugate with respect to K^2 ; so these rays will intersect K^2 and now ensues the theorem:

“The rays of the congruence (2,2), which is the section of the complex with the focal system, have a point in common with the conic K^2 ; so they are found as rays of A cutting K^2 .”

So the congruence (2,2) arising from this belongs to those congruences, not possessing a focal surface, but a singular or double curve¹⁾, geometrical locus of the first series of foci of the congruence.

6 The congruence can be constructed as a whole out of points of the conic K^2 ; for these points have the property of being the points of intersection not only of two but of a whole pencil of rays of the congruence (2,2), situated in the focal planes belonging to each of the points. These focal planes envelop a quadratic cone P^2 , with the vertex P ; so the congruence must touch the cone. From this ensues the following construction:

“Let a point A be taken on K^2 , the focal ray PA be drawn, cutting K^2 for the second time in A' . Let the two tangential planes to P^2 be brought through PA ; each of these planes contains a pencil of rays of the congruence, the vertex of one pencil being A , of the other A' .”

7. We now proceed by giving some visible properties of the congruence (2,2).

a. The two foci of each ray are the points of intersection with K^2 and the point of contact with P^2 . The focal surface of points becomes P^2 ; the focal surface of tangential planes consists of the tangential planes of K^2 .

b. All rays of the congruence (2,2) belonging to a congruence of rays (1,1) of A cut two conjugate polars of A , and cutting at the same time K^2 they form a ruled surface of order four with a simple conic and two double lines.

c. The rays of the congruence (2,2), lying on a hyperboloid of

¹⁾ Congruences of this type are ranged in the “Index du répertoire bibliographique des sciences mathématiques” under $N^2 1 e x$ and placed by R. STURM in a separate division; see “Liniengeometrie”, II, p. 323.

\mathcal{A} , pass through the points of intersection of the latter with K^2 , so they are four in number.

d. Let K^2 be real and let P be situated within K^2 ; all focal rays through P , the focal point of plane PRS , now cut K^2 ; so all pencils of rays are real. If P lies outside K^2 two tangents out of P can be drawn to K^2 ; these tangents are the lines of intersection of the cone P^2 with plane PRS . The planes touching P^2 according to these lines of intersection are focal planes, in which two pencils of rays have coincided; rays through P , not cutting K^2 , give rise to imaginary pencils of rays of the congruence (2,2). Further ensues from this:

“If K^2 is real and all the vertices of the tetrahedron of coincidence likewise are real, the congruence (2,2) is built up of real and imaginary pencils of rays, where as a transition two are double ones; if K^2 is real but the vertices R and S are imaginary, all the pencils are real.”

e. The cases in which K^2 is imaginary, or also those in which all the vertices of the tetrahedron of coincidence are imaginary, do not give real congruences; so they are not under consideration.

8. We now pass to the representation of the congruence (2,2) by which the image is obtained of the connection of focal system and tetrahedral complex.

a. The congruence containing ∞ pencils of rays which are represented in Σ_1 by straight lines having a point in common with X_1^2 , the whole congruence is represented by a ruled surface passing through X_1^2 . To a straight line l_1 in Σ_1 a hyperboloidic system of focal rays corresponds, which has four points in common with K^2 ; so it contains four rays of the congruence and the representing surface S_1^4 of the congruence (2,2) is a ruled surface of order four.

b. An arbitrary pencil of focal rays of \mathcal{A} contains two rays of the congruence; the straight line in Σ_1 corresponding to them cutting X_1^2 has another two points in common with S_1^4 ; so X_1^2 is a double conic of S_1^4 .

c. To the pencil of rays in Σ with P as vertex and PRS as plane a straight line μ_1 in Σ_1 corresponds, cutting X_1^2 . Each ray of the pencil P/PRS belonging to two pencils of rays whose vertices are points of intersection with K^2 , in all points of μ_1 two generators of S_1^4 concur; from this follows that S_1^4 is a ruled surface having as double curve a conic with a straight line cutting it; with this the type of S_1^4 has been established.

9. A closer acquaintance with the form of S_1^4 is obtained by tracing the pinchpoints on the double curve; there can be two of them on p_1 and two on X_1^2 . Those of p_1 depend on the position of P with respect to K^2 .

a. Let P be outside K^2 . When a ray through P cuts K^2 in two points, we get two pencils of rays of the congruence, to which two real generators of S_1^4 correspond, concurring in a point of p_1 . For the tangential lines out of P to K^2 these two generators coincide, so the point of S_1^4 , from which they are drawn is a pinchpoint; so for this position there are two real pinchpoints on p_1 ; from this ensues:

“If P lies outside K^2 , p_1 has one part appearing as double line and another which is isolated; two pinchpoints separate these two parts.”

b. Let P lie within K^2 . All focal rays through P cut K^2 ; there are no tangents to K^2 , so there are no pinchpoints on p_1 . So the double line p_1 is in its whole length really double line.

Besides the pinchpoints on p_1 the surface S_1^4 has also pinchpoints on X_1^2 . To find these we must keep in view that the points on X_1^2 correspond to the pencils of rays whose vertices lie on $XX' \equiv x$, which are thus situated in planes through x . Let γ be a plane through x and C its focal point; the pencil of rays $(C\gamma)$ has two rays cutting K^2 viz. the two rays connecting C and the points of intersection B and B' of γ and K^2 . These two rays are represented in Σ_1 by a single point B_1 of X_1^2 . Now CB belongs still to another pencil of focal rays, viz. to the pencil whose vertex is B and whose plane is the plane $CBP \equiv \beta$. The latter pencil belongs to the congruence (2,2) and is thus represented by a straight line through B_1 lying on S_1^4 . In a similar way it appears that also a second straight line of S_1^4 passes through B_1 , namely the one which is represented by the pencil of rays $(B'\beta')$ lying in plane $CB'P$. Now again two principal cases may occur:

a. x cuts the plane PRS in a point T outside K^2 . The pencil of rays T lying in this plane has rays cutting K^2 in two points, touching K^2 or having two imaginary points in common with K^2 . In this case these are parts of X_1^2 through which two generators of S_1^4 pass, which have thus to be regarded as points of a double curve, and parts which are isolated; the transition is formed by two pinchpoints, through which two coinciding generators pass; and these last correspond to the pencils of rays, having their vertices on the tangents drawn from T to K^2 .

b. The above mentioned point of intersection T lies within X_1^2 . All rays through T cut K^2 ; through each point of X_1^2 two generators pass, so the whole conic X_1^2 is a double curve.

10. Among the particular sections of S_1^4 the conics of this surface come into account. These conics have two points in common with X_1^2 ; so (3) to these must correspond in Σ hyperboloidic systems of focal rays of \mathcal{A} . These can be constructed in the following way:

Let again a point \mathcal{A} be taken on K^2 , its focal plane α be determined, moreover the second point of intersection \mathcal{A}' of α with K^2 and the focal plane α' of \mathcal{A}' . If now a pencil of rays be drawn in α' through \mathcal{A} (which rays are not focal rays) and likewise through \mathcal{A}' in α , the pencils (\mathcal{A}, α') , (\mathcal{A}', α) consist of conjugate polars of \mathcal{A} between which a projective correspondence is established by means of the focal rays. In connection with X_1^2 each pair of conjugate polars causes a hyperboloidic system of focal rays to appear. These two pencils generate them all, so their number is ∞ .

11. Finally a few particular cases ask for our attention.

a. The line of intersection x cuts the plane PRS in a point of the tangent plane PR . The pencil of focal rays in the plane PR has as vertex this point of intersection; to this pencil corresponds a pinchpoint on X_1^2 , but at the same time this pencil of rays has moreover a ray in common with the pencil of rays in the focal plane of the point R ; so the obtained pinchpoint is at the same time a point of p_1 ; from this follows that in the point of intersection of X_1^2 and p_1 two pinchpoints have coincided; so through this point only a single generator of S_1^4 can be drawn.

b. Application to the motion of an invariable system. In this case K^2 is imaginary (the imaginary circle in the plane at infinity); so the congruence (2,2) consists entirely of imaginary rays. The pencil of rays P/PRS , however, remains real; so the representation in Σ becomes an imaginary ruled surface S_1^4 with real double curve consisting of a straight line and a conic intersecting it. The same observation can be made for other cases where K^2 becomes imaginary.

c. Another particular case occurs when the ray $XX' \equiv x$ is taken in such a way that it cuts the conic K_1^2 ; by doing so the character of the congruence does not change, but its representation does. If we now consider a pencil of rays in a plane brought through x , it is apparent that always one of the two rays of congruence to K^2 coincides with x . Of the two rays cutting in Σ_1 the double conic X_1^2 only one is situated on S_1^4 , the other one passes into a ray situated in ξ_1 ; from this follows:

^uWhen the focal ray x cuts the conic K^2 the surface S_1^4 breaks up into ξ_1 and a cubic ruled surface S_1^3 of which p_1 is a double line; so this gives a simpler representation of the congruence (2,2)

Physiology. — “A new law concerning the relation between stimulus and effect.” By Dr. J. K. A. WERTHEIM SALOMONSON, communicated by Dr. C. WINKLER. (Communication IV).

In three papers, bearing the title “a new law concerning the relation between stimulus and effect I, II and III, I have tried to prove that by increasing a stimulus, the effect too will increase in a definite manner.

The relation was expressed by the formula

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

In deducing this formula I assumed that the transformation of chemical substance caused one and only one well-defined effect.

In most cases however from such a transformation several consequences will result, constituting together the total effect: e.g. a mechanical, a thermal, a chemical, an electrical effect may be caused simultaneously by some changing of the protoplasm.

The question arises, whether our mathematical expression may be applied as well to the different parts of an effect as to the total effect. In order to obtain an answer to this question, we have to consider again the differential equation:

$$- dE = BE dR \dots \dots \dots (2)$$

expressing, that by an infinitesimal increment of stimulus an infinitesimal proportional part of the transformable substance was transformed, and at the same time stating the quantity of this transformation. The quantity $- dE$ represents the increment of the effect. In the case of the effect being composed of several different parts, the same equality will prevail for any of them, e.g. the $\frac{1}{n}$ part, and so we shall obtain for a *partial* effect the equation

$$-\frac{1}{n} dE = BE dR \dots \dots \dots (3)$$

in which $n > 1$.

From this formula we get the expression

$$E = a \{ 1 - \epsilon^{-nB(R-c)} \} \dots \dots \dots (4)$$

wherein a represents another constant than A , and wherein n is a number larger than 1.

This formula for a partial effect is identical to the formula for a

total effect the only difference being that the exponential constant in the case of a partial effect is larger than in that of a total effect.

The muscle may be taken as an example. Every contraction brings about a mechanical effect, whilst at the same time an electrical response is given. Finally the production of heat may be taken for the total effect, at any rate in the case of isotonic or isometric contractions where the mechanical effect is afterwards converted into heat. Thence we are justified in presuming that our statement about the formulæ for total and partial effects, may be applied to the thermal effect and mechanical effect of muscle-contractions.

I have tried to ascertain whether the numbers, given for the thermal-effects by different authors are in accordance with our law.

In DANILEWSKY¹⁾ I found several series of numbers, from which the following tables were calculated



T A B L E I.

DANILEWSKY, l. c. pag. 184.

Isometrical contraction. Initial
load 40 gram fig. 1. $A = 23$ $B = 0.03$ $C = 18$.

R	E_w cal.	E_w observ.
20	1.54	1.7
30	6.97	4.5
40	11.09	11.4
50	14.18	16.2
80	19.38	19.2
100	21.00	19.8
300	22.98	20.5
600	23.	22.
800	23.	24.2

In this table, as in the following R represents the magnitude of the stimulus; E_w observ. the thermal effect as observed by DANILEWSKY.

¹⁾ B. DANILEWSKY. Ergebnisse weiterer thermodynamischer Untersuchungen der Muskeln. V. e. A. FICK. Myothermische Untersuchungen 1889.

E_w calc. the thermal effect, as calculated with the constants given at the head of each table.

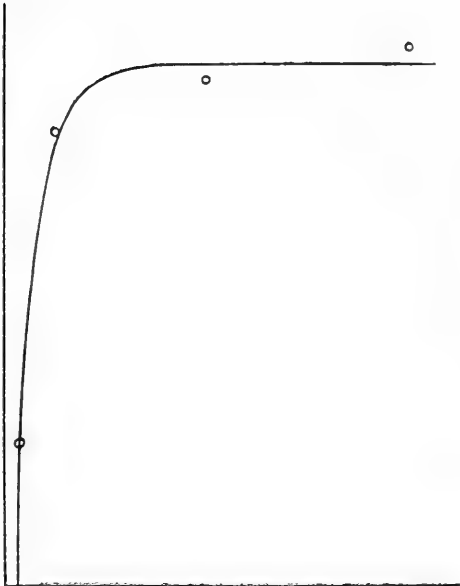


T A B L E II.

Ib. Initial load 80 Gr. fig. 2.

 $A = 24.2$ $B = 0.0324$ $C = 20.$

R	E_w calc.	E_w observ.
30	6.7	6
50	45.3	48
100	22.4	21.7
300	24.2	24.8



T A B L E III.

Ib. Initial load 300 Gr.

fig. 3.

 $A = 20.8$ $B = 0.0217$ $C = 16.4.$

R	E_w calc.	E_w observ.
30	5.3	5.5
100	17.4	18
400	20.7	20
800	20.8	21.5

The first of the next-following tables, which are much more important, is also taken from the experiments of DANILEWSKY i.e.,

whilst the observations in the 5th and 6th table have been published by NAWALICHIN¹⁾: the school of HEIDENHAIN and that of FICK are both represented.

The higher importance of the series given hereafter, consists chiefly in the fact of their having served to determine as well the mechanical response as the thermal effect with stimuli of increasing magnitude.

In the series of DANILEWSKY a double thigh-muscle-preparation of the frog after the method of FICK was employed, whilst NAWALICHIN made use of a single gastrocnemius.

The muscle contracted isotonically, whilst simultaneously the thermal and the mechanical effect of each contraction, were recorded. As it has been proved with sufficient accuracy in our first papers that our formula may be applied to isotonic twitches, these may now serve us as a means of control.

In the following series the magnitude of stimulus is again indicated in the first column by R . The second column contains the calculated height of twitch, the third column the observed height; the fourth column the calculated and the fifth the observed thermal effect. The constants A_w , B_w and C_w were used for calculating the thermal effects, the constants A_h , B_h and C_h for calculating the heights of the contractions.



TABLE IV.

DANILEWSKY l. c. Load 60 Gr. fig. 4.

$A_h = 40$ $B_h = 0.05$ $C_h = 14.4$
 $A_w = 14.55$ $B_w = 0.02$ $C_w = 14.4$

R	E_h calc.	E_h observ.	E_w calc.	E_w observ.
20	9.77	9.8	1.54	0.7
30	21.66	27.7	3.90	4
50	33.25	33	7.41	7.7
100	39.45	39.1	11.92	11.1
300	40.00	40	14.50	14.5

¹⁾ NAWALICHIN, Myothermische Untersuchungen. Pflüger's Archiv, Bd. 14, p. 297.

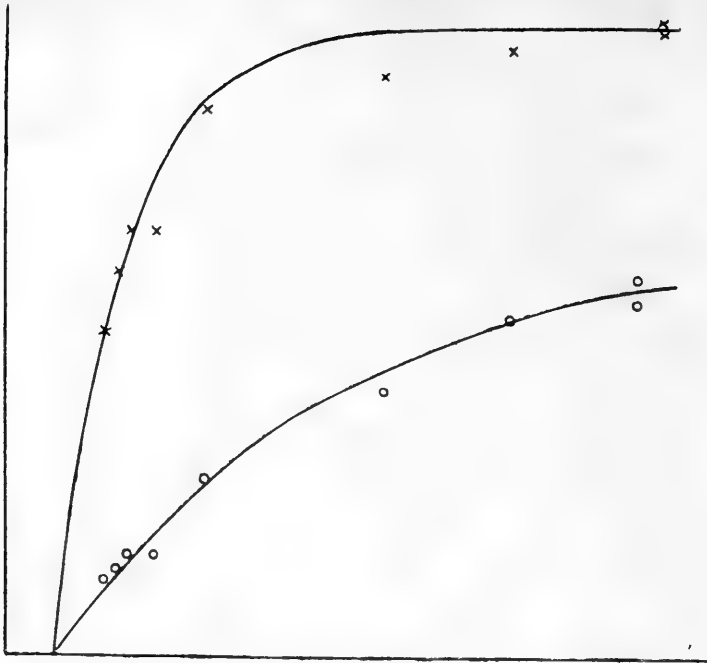


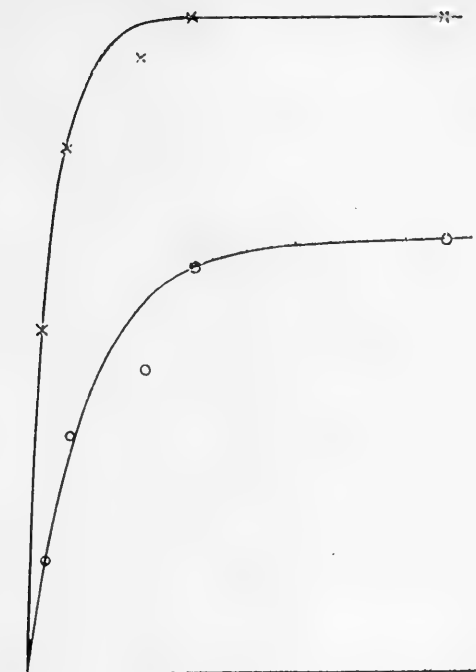
TABLE V.

NAWALICHIN l. c. pag. 297. Load 30 Gr. fig. 5.

$$A_h = 6.25 \quad B_h = 0.0036 \quad C_h = 205$$

$$A_w = 17. \quad B_w = 0.00085 \quad C_w = 205$$

R	E_h calc.	E_h observ.	E_w calc.	E_w observ.
40	3.17	3.2	2.60	3
45	3.66	3.8	3.20	3.5
50	4.08	4.2	3.78	4
60	4.74	4.2	4.81	4
80	5.52	5.4	6.75	7
150	6.18	5.7	11.34	10.5
200	6.23	6	13.30	13.5
250	6.25	6.2	14.60	15
250	6.25	6.3	14.60	14



T A B L E VI.

lb. Load 90 Gr. fig. 6.

$$\begin{array}{lll}
 A_h = 6.5 & B_h = 0.0185 & C_h = 660 \\
 A_w = 17.15 & B_w = 0.008 & C_w = 660
 \end{array}$$

R	E_h calc.	E_h observ.	E_w calc.	E_w observ.
700	3.40	3.5	4.70	4.5
750	5.27	5.3	8.80	9.5
900	6.42	6.4	14.61	12
1000	6.50	6.5	16.00	16
1500	6.50	6.5	17.40	17

Considering that the degree of accuracy with which the thermal effects were measured is not very high, we have some cause for satisfaction about the results of our calculations. Though only a first approximation has been effected throughout all these series, the errors remain wholly within the limits of the mean errors of observation. Moreover in some cases it is even possible to apply a correction.

Looking at series VI, we see immediately that the observed numbers

corresponding to the stimulus 900 are rather too small, as well for the height of twitch as for the heat-production. Calculating from the observed lifting-height the corresponding magnitude of stimulus, we find 810 instead of 900. Now taking this number 810, to calculate the heat-production, we obtain 12, in perfect accordance with the observation. The supposition that the number 900 is an error and that 800 was meant is not very hazardous.

From the communicated series we may draw firstly this conclusion that the heat-production, considered as total effect, increases virtually with increased magnitude of stimulus in the manner indicated by the established formula.

In the three last series B_w , the increment-constant for the thermal effect, proved to be always smaller than the B_h corresponding to it, a fact predicted already in our deduction. We found for the number $n = \frac{B_h}{B_w}$ in series IV, V and VI the value 2.5, 4.23 and 2.31. Though of course even by this fact our deduction may not be deemed absolutely proven, it nevertheless affords a valuable support for considering the deduction proposed by me as a most useful working-hypothesis.

Bacteriology. — “*On a colourless bacterium, whose carbon food comes from the atmosphere.*” By Prof. M. W. BEIJERINCK and A. VAN DELDEN.

We give the name of *Bacillus oligocarbohilus*¹⁾ to a colourless bacterium, whose carbon nutrition in the dark (and likewise in the light), takes place at the expense of a not yet well-known atmospheric

¹⁾ It is probable that W. HERAEUS (Ueber das Verhalten der Bacterien in Brunnenwasser sowie über reducirende und oxydirende Eigenschaften der Bacterien. Zeitschrift f. Hygiene, Bd. I, pag. 226) already in 1886, has had cultures of *B. oligocarbohilus* before him. He says the following: . . . „Ausserordentlich auffallend war das Ergebniss dieser Versuche in der Hinsicht, dass eine Vermehrung der Bacterien in einer Flüssigkeit eingetreten war, welche keine organische Verbindungen sondern nur Salze enthielt. Ein unansehnliches, kaum sichtbares Pünktchen von Bacterienzoogloëen hatte sich im Verlaufe vom zehn Tagen so stark vermehrt, dass die ganze Oberfläche der Lösung von einer dicken Haut bedeckt war.” Analytical results are not given, and the remark makes the impression of being accidental and is lost among insignificant observations. — WINOGRADSKY'S statement, concerning the accumulation of organic carbon in nitrifying solutions, evidently refers likewise to this microbe, but his description suffers of indistinctness (Annales de l'Institut Pasteur, T. 4 pg. 270 et 462, 1891).— In the experiments of GODLESWKI (Bulletin international de l'Académie d. sc. d. Cracovie, Dec. 1892 pag. 408 et Juin 1895 pag. 178), the vanished CO² is not, as he thinks, absorbed by the ferments of nitrification but by the Mg O.Mg CO³.

carbon compound (or compounds), from which the energy, wanted for the vital processes, is also derived¹⁾.

The culture of this bacterium on solid media or in nutrient solutions, containing soluble organic substances has not yet succeeded, which may, of course, have been caused by an erroneous choice of these substances. On the other hand, pure cultures on solid and in liquid substrata, without soluble carbon compounds, are easy to be made.

1. CRUDE CULTURES OF BACILLUS OLIGOCARBOPHILUS.

Bacillus oligocarbophilus is obtained by the following accumulation experiment, which, because of the purity of the thereby resulting vegetation, may be called a "perfect accumulation experiment."

Into a large ERLÉNMEYER-flask a thin layer is introduced of a nutrient liquid of the same composition as used for the water culture of higher and lower green plants, but with alkaline instead of acid reaction.

One takes for instance:

Distilled water	100
Kaliumnitrate	0.01 to 0.1
Dinatriumphosphate	0.02
"Mineral solution"	1 drop.

This "mineral solution" contains in one drop:

8	Mgrms	MgSO ₄ . 7 H ₂ O
0.05	"	MnSO ₄ . 4 H ₂ O
0.05	"	FeCl ₃ . 3 H ₂ O

If from this liquid nitrogen, phosphor, kalium or magnesium is left out, special experiments have proved, that no, or but an insignificant growth is obtained. As to the necessity of the likewise added elements sulphur, manganese and iron, there still exists some doubt.

The inoculation is made with a not too small quantity of garden-soil, the flasks are closed with a cotton plug, or with filter paper, without impeding the entrance of air by diffusion, and the culture is left in the dark at 23—25° C. After two or three weeks, the fluid, which itself remains perfectly clear, is seen to cover with a thin, white, or feebly rose-coloured, very dry film, difficult to moisten, and macroscopically resembling a *Mycoderma*-film, but consisting of minute bacteria, microscopically often invisible without staining, and sticking together by a slimy substance. This is *Bacillus oligocarbophilus*.

¹⁾ We also found another, rarer species, belonging to the genus *Streptothrix* COHN, with corresponding properties. It will not, however, be further discussed here.

The growth of the film continues for months, whereby a considerable accumulation of organic carbon may be observed, which is not only visible to the naked eye by the vigorous bacterial growth, but can also be proved by direct weighing, and by a comparison of the permanganate numbers found before and after the experiment, of which some instances are given below.

As there is reason to admit that our bacterium is generally distributed in garden-soil, and was without doubt always present in the crude material used for the inoculation, the failing of the film-formation in some of the flasks must necessarily result from the chosen culture fluid being less favorable to the feebler germs and not allowing their growth. So we observed that water, distilled in a copper apparatus, caused many more failures than when distilled in glass; we therefore afterwards always used the latter. In other cases monads, which immediately devoured the bacteria, were cause of the failure; by transfers and by the use of pure cultures, these voracious organisms could be rendered harmless or removed. When the distilled water is replaced by tap-water, the number of flasks remaining without growth after inoculation with the same quantity of garden-soil is much smaller.

If once a pellicle has formed, transfers into the said culture liquid, prepared either with distilled or with tap-water, come easily and without exception to development.

2. SOURCE OF NITROGEN REQUIRED.

In the above mentioned nutrient liquid we have chosen kalium-nitrate as source of nitrogen. As well, however, kaliumnitrite or some anorganic ammonium salt may be used. Very good results were obtained with:

Distilled water	100
Ammonium sulphate (or NH_4Cl)	0.01—0.1
Dikaliumphosphate	0.02
“Mineral solution”	1 drop

and with:

Distilled water	100
Kaliumnitrite	0.01—0.1
Dikaliumphosphate	0.02
“Mineral solution”	1 drop.

As both these liquids answer to the conditions of life of the microbes of nitrification, the formation of nitrite or nitrate is actually to be observed when using them, and when inoculating with garden-soil or with crude cultures. With the easily produced pure cultures

of *B. oligocarbohilus*, of which more below, a good development of the film is possible, by which experiment it can at the same time be proved, that this microbe itself does not nitrify. Hence, ammonium salts or nitrites, added to excess can, even for a year or longer, continue unchanged under the luxuriantly growing pellicle of *B. oligocarbohilus*, whereas, in the presence of nitrifying ferments, they completely disappear in a few weeks, being then found back as nitrates. If the ferments of nitrification alone are present, there is no question of film-formation and the nutrient solutions remain perfectly clear.

Not only the nature of the nitrogen-furnishing substances, but also their quantity can in these experiments, as already inferred in the recipes, vary between fairly wide limits, and the same may be said concerning the conditions for the water culture of higher and lower green plants. The limits allowable for *B. oligocarbohilus*, have not yet been precisely fixed, but they certainly have a broader range for this organism (circa 0.1—10 pro mille) than for the higher plants (0.5—5 pro mille).

By many experiments it was established, that in absence of kalium, phosphor, and magnesium, a still slighter growth occurs, than when no nitrogen compounds are given. Evidently *B. oligocarbohilus* finds in the atmosphere, in a condition fit for nutrition, a quantity of nitrogen, which, although insufficient, should not be overlooked.

If the distilled water in the artificial solution is replaced by tap-water, a somewhat higher rate of organic substance is produced. As in tap-water a small quantity of nitrogen compounds occur, — here, at Delft, about 0.4 milligrams of combined nitrogen per litre, whilst it contains the other necessary elements (phosphor and kalium, of course, excepted) in an obviously favorable form for the nutrition of our mikrobe, one can simply use for its culture:

Tap-water	100
Dikaliumphosphate	0.02.

It should, however, be kept in view, that the productivity in bacterial substance, in consequence of the film formation, is not determined by the volume, but chiefly by the extent of the surface of the medium, which is in free contact with the air. Hence, in a very thin layer of tap-water, the nitrogen may soon be consumed, whereas, with the same amount of nutrient liquid, but with a smaller surface, consequently in a thicker layer, the provision of nitrogen will suffice for a longer time. Therefore, in order to obtain from a flask of determined size, the maximum production of *B. oligocarbohilus*, a

nitrogen compound should be added when a small quantity of tap-water is used, which addition is not necessary when cultivating in a greater quantity in a flask of the same size.

3. PURE CULTURE.

Our bacterium does not grow at all or only to a slight extent on the commonly used bacteriological media, these containing too much organic food. But it is easy to produce pure cultures on solid media, when observing the same precautions which I described in the Meeting of the Academy of 27 June 1892 for the pure culture of the ferments of nitrification on agar-plates¹⁾, and to which I referred in the Meetings of 30 March 1901 (Proceedings p. 586) and 25 May 1901 (Proceedings p. 5) when discussing the culture conditions of the oligonitrophilous Cyanophyceae.

In all these cases it is necessary as completely as possible to remove all soluble organic substances from the solid medium, which is to be effected by a prolonged washing with distilled water. The agar thus prepared, with the required nutrient salts, for instance in the proportion:

Distilled water	100
Agar	1.5
K ₂ HPO ₄	0.01
KNO ₃ (of NH ₄ Cl)	0.01

is boiled and plated, and used for strew-or streakcultures originating from a film of *B. oligocarbohilus*. Very soon the common saprophytic bacteria which never lack in the film, are seen to develop on the plate and when these by their growth and respiration have consumed the soluble carbon compounds, which were not yet removed from the agar by the extraction with water, *B. oligocarbohilus* itself begins to grow. This is usually the case after 14 days. Then, however, the colonies become easily recognisable, our bacterium being the only species which in the given circumstances can feed on the atmospheric carbon, and so go on growing, whilst the growth of all other species soon comes to a stop.

Even the colonies of the nitrifying ferments, which, as I have demonstrated before (l. c.), can grow fairly well on this medium, when instead of nitrate an ammonium salt is used, remain very small, never exceeding 1 mM. or less. On the other hand, the colonies of *B. oligocarbohilus* attain dimensions of 1 cM. and more and may then easily be transferred in a pure condition into test-tubes

¹⁾ Nature, Vol. 46, pag. 264, 1892.

on the said medium. They grow on the agar as thin, snow-white or rosy-tinted, very dry, flatly extended layers, which strongly remind of the pellicle floating on the liquid.

Also on silica plates, prepared in glass dishes, which, after extraction of the chlorides are soaked with a nutrient solution, *B. oligocarboophilus* can produce very fine cultures, appearing after some weeks, as snowwhite colonies with indented margin, and which by a right selection of the salts, can finally spread over the whole plate. Then the remarkable phenomenon is observed, that the silica liquefies a little in the centre of the colonies and sinks in by evaporation.

The silica plates are made as follows. A commercial solution of potassium silicate, diluted with a known quantity of water, is titrated with normal hydrochloric acid. As the solidification is much favoured by an alkaline reaction, a complete neutralisation at the preparation of the plate should not occur, and as a plate, with a high percentage of silica, contracts strongly after coagulation, and expresses much water, the dilution must be sufficient for this contraction to be delayed. Into a small beaker-glass was introduced, in a certain case, 5 cM³ of potassium silicate diluted with 25 cM³ of water, and into a second glass the required quantity of hydrochloric acid, amounting to 10 cM³ of normal acid. The acid is mixed with the diluted silicate and the mixture poured into a glass dish. The solidification delays the longer as the mass is more diluted, but it is easy, after some practice, to make very solid plates. The plate is first freed from the chlorides by streaming tap-water, then washed out with boiled water, and afterwards treated with the solution of nutrient salts. When these have sufficiently diffused into the plate, the glass dish is gently warmed at the underside, until the adhering water has evaporated and the plate shows a "dry", glossy surface. The surface is flamed in the BUNSEN-burner, by which only a partly but sufficient sterilisation is to be attained.

Not only *B. oligocarboophilus*, but also the ferments of nitrification grow on this medium very well. By mixing of the diluted solution of the silicate with chalk, magnesium carbonate, or ammonium-magnesium phosphate, snow-white plates may be obtained, which are particularly fit for the culture as well of all these microbes as of several lower algae. Even earth-diatoms, of the genus *Nitzschia* will grow thereon.

Once more it must be observed, that in the silica plates organic substances must be absent, even fragments of cork, fallen into the silicate solution, may disturb the experiment.

The pure cultures, obtained on agar or silica plates, are as well fit

for the further experiments on liquid media as the crude cultures, of which many experiments, continued for years, have convinced us. Every thought of symbiotic relations on which the carbon assimilation by our bacterium might repose is thereby excluded, so that at least the biological side of this part of our problem is clear.

Concerning the further properties of our bacterium in pure cultures, we can be brief. In the films, as well as on in the colonies on the solid media, it consists of minute, thin and short rodlets, probably always immobile. They are ca. 0.5μ wide and $0.5-4 \mu$ long. The length however is very variable and frequently particles are seen 0.5μ wide and $0.7-1 \mu$ long. Often, when not using reagents, such as dyeing substances or acids, no structure at all is to be observed, neither in the colonies nor in the flowing pellicle, but the bacteria at once become visible by staining the preparations. The thick cell-walls form the chief constituent of the colonies; albuminous matter is only present in a slight quantity in this bacterium.

4. THE NUTRITION WITH ATMOSPHERIC CARBON.

A good appreciation of the carbon accumulation may be had as well by a direct weighing as by the permanganate method.

For both determinations it is possible, to suck off the fluid, which is practically free from bacteria, wholly or partly from beneath the film, so that the quantity of the culture material, destined for the filtration or the determination of the permanganate number, is not too voluminous.

In our experiments there only resulted a precipitate of calcium-phosphate or calciumcarbonate, when we had used our tap-water, which is rich in lime, and when kaliumphosphate to excess had been added. These precipitates can, however, be dissolved beneath as well as in the film by dilute acid, and then the acid can be expelled by further washing. The film is so dry and wetted with so much difficulty, that all these manipulations may be effected without much loss of material.

The permanganate number was determined after KUBEL's¹⁾ method.

In relation to the quantity of organic matter found by direct weighing or by the permanganate method and formed from the atmospheric carbon, the following should be well observed.

As *B. oligocarbophilus* grows only on the free surface of the

¹⁾ TIEMANN-GÄRTNER'S Handbuch der Untersuchung der Wässer, 4e Aufl. pag. 255 1895.

medium, and not in the depth, the thickness of the layer of the nutrient solution and consequently its volume, is, as already observed, actually indifferent. That is to say, by enlarging the surface of the solution, a bacterial film of any dimensions is to be obtained, which circumstance is of importance for appreciating the productivity of a certain quantity of a nutrient solution, the more so as the thickness of the bacterial film is usually only one cell-layer. How very thin the required thickness of this layer can be, growth being still possible, may be derived from the fact, that, especially when using distilled water with nutrient salts, the film can mount at the apparently dry glass-wall from 1 to 1.5 decimeter high, and not seldom extends on it nearly to the cotton plug. Only in certain vinegar bacteria I observed the same.

As it seems that our bacterium forms no compounds prejudicial to its growth, so the only circumstance, which governs its increase relatively to a given volume of liquid, provided its surface be of a sufficient extent, is the lack of one or more elements necessary for the nutrition. Carbon cannot be among the number, our experiments being made with free entrance of air.

Although it is thus established, that only the number of bacteria, produced in a certain time per surface-unit, indicates the rate at which the atmospheric carbon is assimilated, we will yet give the quantities in relation to the volume of the solution, because then a comparison can be better made with the numbers found by other authors for polluted waters.

5. HOW MUCH CARBON IS ASSIMILATED.

First we determined by an experiment, in which, after vigorous shaking, a culture was divided into two equal portions, how much one half contained at direct weighing, of bacterial substance, whereas the other half was titrated with kaliumpermanganate. We used for this a three months old culture on :

Tap-water	100
Na ₂ HPO ₄	0.02
KCl	0.02
KNO ₃	0.02

The film from the part, destined for the weighing, was separated from the liquid by filtration, washed out on the filter with strongly diluted hydrochloric acid, and subsequently with distilled water, to remove the chlorids. Subsequently the filter with the film was

dried, first at 40°—50° C. and then at 100° C., until the weight remained constant. So we found that per litre 180 milligrams of bacterial matter were produced, and that, after deduction of 14 milligrams, used by a litre of our tap-water itself, the corresponding permanganate number was 94. We can thus, with an accuracy sufficient for our purpose, accept that the relation between the two figures is as 2:1, that is to say, that the doubling of the permanganate number gives the weight of the dry bacterial substance, and, as this latter number is much more quickly to be found than the weight, we have contented ourselves with it in most of our further determinations.

We shall now give some more figures. Like the preceding they all relate to bacterial films produced in ERLENMEYER-flasks on 100 cM³. liquid with a free liquid-surface of about 80 cM².

By weighing we found in one case on:

Tap-water	100
KCl	0.02
KNO ₂	0.02
K ₂ HPO ₄	0.04

after 5 months' culture 235 milligrams per litre. On:

Distilled water	100
KCl	0.02
KNO ₃	0.1
K ₂ HPO ₄	0.02
"Mineral solution"	1 drop

after 5 months 220 milligrams per litre.

Some numbers, found by the permanganate method follow, and in the first place some relating to tap-water.

The greatest production which we had, was obtained with tap-water 0.02 K₂HPO₄ and 0.02 KNO₃, after a year's culture and amounted to 250 mgrs. of permanganate per litre, nearly corresponding with $250 \times 2 = 500$ milligrams of dry bacterial substance.

After a shorter time the production is likewise smaller; so we found in a culture on:

Tap-water	100
Na ₂ HPO ₄	0.02
KCl	0.02
KNO ₃	0.02

after 5 months' culture (January to May) 202 mgrs. of permanganate, corresponding with 404 mgrs. of bacterial matter per litre.

If the tap-water was replaced by distilled water, the production of dry organic substance was commonly smaller, which cannot, however, result from the nutrition by substances in the tap-water, oxidisable by kaliumpermanganate, for the 14 mgrs. of permanganate, which our tap-water consumed per litre, we found quantitatively back, at the end of the cultivation period, in the clear liquid beneath the pellicle of *B. oligocarbophilus*, which liquid can easily be sucked off with a pipette, without any considerable bacterial contamination. Moreover the experiments with distilled water have likewise exhibited great divergency in production, and though the cause has not been established with perfect certainty, we still think it probable, that these differences result from the greater or smaller density of the cotton plugs, by which the speed of air entrance is greatly influenced. We base this supposition on results obtained with flasks, only differing in the width of the mouths, and to which we shall refer later. It is furthermore certain that we have not to do here with the infection of other bacteria, or with monads, for the pure cultures displayed as considerable divergency as the crude ones. Neither can the chief cause be attributed to a change in percentage of the air in gaseous carbon compounds, the differences being observed simultaneously in cultures placed side by side in the same locality.

But we now give some further numbers. In an experiment with:

Distilled water	100
K_2HPO_4	0.02
KNO_2	0.1
KCl	0.01
“Mineral solution”	1 drop

sterilised and inoculated with a pure culture of *B. oligocarbophilus*, were found, after 37 days' cultivation (2 Jan.—19 Febr.) at 23° C., 66.6 mgrs. of permanganate, corresponding with circa 133 mgrs. of dry bacterial substance per litre.

In another experiment with:

Distilled water	100
Na_2HPO_4	0.02
KNO_2	0.01
“Mineral solution”	1 drop

likewise sterilised and after a culture of 40 days, at 23° C. the permanganate number amounted to 60 mgrs., corresponding with 120 mgrs. of dry bacterial matter per litre.

In a third case in:

Distilled water	100
K_2HPO_4	0.02
$(NH_4)_2SO_4$	0.02
Na_2CO_3	0.01
“Mineral solution”	2 drops

after cultivating from 5 May to 1 Dec., 155 mgrs. of permanganate per litre were found.

In a culture in:

Distilled water	100
Na_2HPO_4	0.02
KCl	0.02
KNO_3	0.02
“Mineral solution”	1 drop

from 1 June to 1 Dec. we found 165.5 mgrs. of dry bacterial substance, corresponding with ca. 83 mgrs. of permanganate per litre. As we see, the differences are considerable.

When a little natrium acetate was added to the anorganic solution, and when using a pure culture for inoculation, we could neither state an augmenting nor a diminishing of growth.

Thus we obtained in:

Distilled water	100
KCl	0.02
KNO_3	0.1
Natriumacetate	0.02
K_2HPO_4	0.02
“Mineral solution”	1 drop

by means of weighing, 220 mgrs. of dry bacterial substance per litre, corresponding with 110 mgrs. of permanganate, which figures are not exceedingly high and might likewise have been produced in the same time (4 months) from the air alone, without acetate.

In all these experiments with distilled water, the free surface of the liquid was also 80 cM², and the air had to pass through a dense cotton plug, with which the ERLÉNMEYER-flasks were closed. Already before we drew attention to the importance of the way in which the flasks are closed; be here still mentioned that we made some special experiments, which proved that a very narrow opening of the flasks, slackens the growth of *B. oligocarboophilus*, so that years may go by before the film has vigorously developed. We could not, however, expect anything else, for the considerable volume of air, required for the growth of the said quantities of bacteria, can only very slowly diffuse inward and outward through the narrow canal.

6. CARBONIC ACID CANNOT SERVE AS FOOD.

Various experiments were made to establish what may be the volatile atmospheric carbon compound which renders the growth of *B. oligocarophilus* possible. That it cannot be carbonic acid, whether free or combined, resulted from the following experiments. In closed culture-flasks with the best nutrient solutions, and arranged in such a way, that at times a little free carbonic acid mixed with pure air, could artificially be introduced, it was not possible to get any growth. This experiment, which seemed of particular interest, has been so frequently repeated, and so long continued under different conditions, that we consider it as quite certain, that free carbonic acid cannot serve for the nutrition of *B. oligocarophilus*.

For testing the influence of combined carbonic acid, cultures were made, firstly in the following solution :

Tap-water	100
Dikaliumphosphate	0.01
Kaliumnitrate	0.01
Natriumbicarbonat	0.1

When cultivating at the free air surely a luxurious growth was obtained, but it was by no means more vigorous than when the bicarbonate was left out.

If in this liquid the nitrate was replaced by an ammonium salt, the result was quite the same.

Secondly, the bicarbonate was replaced by common natrium carbonate, the same quantities of the different salts being used. But in this case the action proved rather injurious than favorable. It is true that the film had become considerable after a few months, but it was directly to be seen that the growth was so much inferior to that of cultures obtained in the same circumstances but in absence of carbonate, that the determination of the permanganate number seemed superfluous. Here, too, the replacing of nitrate by an ammonium salt or by a nitrite caused no change.

As a remarkable fact it may be mentioned, that in these experiments, in our large flasks, containing a litre of air, the thin bacterial film mounted very high up the dry glass-wall, which is likewise often observed in the solutions made with distilled water, and may repose on the absence of dissolved lime salts.

If the tap-water was substituted by distilled water, the addition of natrium carbonate did not cause an increase of bacterial growth either. We found, for instance, in :

Distilled water	100
K_2HPO_4	0.02
$(NH_4)_2SO_4$	0.02
Na_2CO_3	0.1
"Mineral solution"	1 drop

after 7 months (5 May—1 Dec.) 155 mgrs. of permanganate, corresponding with ca. 300 mgrs. of dry bacterial substance per litre, which production is less than that, obtained in other cases under the same circumstances but without carbonate, so that here also, the action of the carbonate, the long time of cultivation being taken into consideration, was not favorable. Quantities of carbonate, smaller than 0.1 %, were neither successful.

The results of this examination can be thus summarised, that for the growth of *B. oligocarbophilus* an atmospheric carbon compound is actually consumed, but that this cannot possibly be free carbonic acid. Furthermore, that also combined carbonic acid cannot serve for its nutrition.

7. NATURE OF THE ASSIMILATED ATMOSPHERIC CARBON COMPOUND.

If the carbonic acid of the air cannot be the food of *B. oligocarbophilus*, what other atmospheric carbon source might then come into consideration?

It is clear, that we should think here of the carbon-containing component of the air, discovered in 1862 by the botanist HERMANN KARSTEN ¹⁾, and recently discovered anew by French experimenters, especially by Mr. HENRIET ²⁾. It is true that the chemical nature of this substance has been hitherto unknown ³⁾, but yet it is certain that we have here to do with an easily oxidisable compound (or compounds), for a prolonged contact with alkali and air will already suffice to split off carbonic acid from it. Furthermore, according to the statement of the French investigator, the substance probably contains nitrogen.

This latter circumstance gives rise to the question whether this

¹⁾ H. KARSTEN. Zur Kenntniss des Verwesungsprocesses. Poggendorff's Annalen Bd. 191, pag. 343. 1862. To this place, as also to the not unimportant older literature on the carbon compound of the air, my attention was drawn by Mr. G. VAN IJERSON.

²⁾ Comptes Rendus T. 135, pag. 89 et 101. 1902.

³⁾ HENRIET thinks that the substance must be a monosubstituted formamid with the formula $HCO.NHR$, where R represents a still unknown alkylrest. But then it is not easy to understand, why the production of carbonic acid takes place so readily. It might then rather be expected that, with an alkali a formiate would result and no carbonate.

nitrogen, like the carbon, is fit for assimilation by our microbe. Though this question has already partly been answered in the negative by the preceding experiments, it should still be remarked here that in nutrient liquids, without an expressly added nitrogen compound, for instance in:

Distilled water	100
K_2HPO_4	0.02
Mg, S, Mn, Fe	traces.

Or still better in:

Tap-water	100
K_2HPO_4	0.02

without any further addition, a not inconsiderable growth of *B. oligo-carbophilus* may occur, so that at least traces of an assimilable nitrogen compound may be drawn from the air by this bacterium, whereas, for the possibility of assimilation of the free atmospheric nitrogen no indications were found.

We now turn to another question, which the assimilation of the atmospheric carbon gives rise to, namely: How great is the quantity of the volatile substance wanted for the formation of the bacterial film produced in our cultures? This question is closely connected with the following: How much of the compound is moreover consumed by the respiration of our bacterium, escaping as free carbonic acid? For answering these questions we have to measure the quantity of the carbonic acid corresponding with a determined weight of dry bacterial substance, granted that the carbon percentage of this substance be known.

Our experiments relating to the measurement of the quantity of carbonic acid produced, are not yet closed, but as to the first part of the question, we give the following calculation to fix the volume of air wanted for the production of the carbon, actually accumulated in the bacterial films. We hereby make two chemical suppositions which, to be sure, are fairly well in accordance with truth. First, we admit that the carbon, freed from the unknown compound, as carbonic acid by a prolonged contact with alkali, is consumed quantitatively by our bacterium and, secondly, that the bulk of the bacterial cells consists of a substance possessing nearly the composition of cellulose¹⁾.

¹⁾ If accepting that the composition of the bacterial cells corresponds with that of albuminous substances, then, instead of 44% C., 52 to 55% C. should be brought into account, and in this proportion the volume of the air should be augmented.

Let us now consider the case when, in $\frac{1}{2}$ litre-flask with 100 cM^3 . of fluid and a free surface of 80 cM^2 , after a month's culture a quantity of 20 mgrs. of dry bacterial substance is formed, which, calculated as cellulose, contains 44 % C.; we then find in the 20 mgrs. of dry matter 8.8 mgrs. of carbon. According to HENRIET the atmospheric carbon compound, present in a certain quantity of air, under prolonged action of alkali, gives out as much carbonic acid as occurs already in a free state in the same volume of air, that is per litre $0.3 \text{ cM}^3 = 0.6$ mgrs., in which 0.163 mgrs. of carbon are present. Thus, for 8.8 mgrs. are wanted 55 litres of air. Consequently, in the course of a month these 55 litres of air must have diffused through the cotton plug inward and outward of our $\frac{1}{2}$ litre-flasks, in order to produce the found quantity of carbon, that is 76 cM^3 . hourly.

Though this figure should not be considered à priori as impossible, it still appears to be very high, and the difficulty of accepting it increases, if still the addition has to be made of a yet unknown, but apparently considerable amount consumed for the bacterial respiration, which, as remarked above, seems necessary. We therefore think that it must be admitted that the quantity of the atmospheric compound (or compounds) assimilable by *B. oligocarophilus*, is much larger in our laboratory atmosphere, than in that of the Paris boulevard, analysed by HENRIET, and that we have here to do with an extremely variable factor. The circumstance, too, that we have not as yet been able in our greenhouse, where the air, in the common sense of the word, is surely much purer than in the laboratory, to obtain a vigorous growth of *B. oligocarophilus* pleads for this view. But here we could not always keep the temperature high enough, so that we consider our experiments in this direction not yet closed. Besides, we should observe, that in an empty, isolated room of the laboratory, the quantities of combined carbon drawn from the air, were as great, or only little less than in the laboratory itself, where the air was certainly impurer.

We are accordingly conscious that further experiments, with fresh atmospheric air are wanted to decide, whether the carbon compound occurs in the atmosphere in a constant or in a varying percentage. Only thereby it will be possible to ascertain the distribution of this compound, by which, at the same time, the signification of *B. oligocarophilus* in nature will become clearer.

As to this signification, the question arises whether our microbe in substrata containing sufficient mineral nutrients (N, P, K, Mg, S, Fe, Mn), but being poor in organic substances, is able to build up the latter in the dark from the volatile carbon compounds occurring in the

atmosphere of the surrounding medium. And furthermore, whether carbon nutrition takes place exclusively in the floating dry films, — hence, in the earth, only on the relatively dry surface of the earth particles, — or that also in the depth of fluids growth and carbon assimilation be possible. The hitherto gathered experience about the self-purification of rivers and the biological purification of water in general, seems to exclude the latter hypothesis, and our own experiments too, render it not probable. The result of these experiments consists, in our opinion, in the very discovery of a microbe, which, in consequence of the film-formation, has the specific faculty, to absorb for its nutrition and multiplication, from a gas, namely the air, traces of volatile carbon compounds, by which the struggle for existence with the rest of the microbial world can be successfully sustained. The biological purification of water would, according to this view, find a counterpart in the biological purification of the air by *Bacillus oligocarbohilus*

Physics. — “The calculation of $\frac{e}{m}$ from the magnetic rotation of the plane of polarisation, for substances without an absorption band in the visible spectrum.” By DR. L. H. SIERTSEMA. (Communication No. 82 from the Physical Laboratory at Leiden by Prof. H. KAMERLINGH ONNES).

Starting from FITZGERALD'S¹⁾ simple explanation of the magnetic rotation of the plane of polarisation derived from the ZEEMAN effect, and also from the supposition that the result of the magnetic force is only shown by the displacement of the dispersion curve of the medium ($n=f(\lambda)$) over a distance d , HALLO²⁾ finds for the magnetic rotation ω

$$\omega = \frac{2\pi}{\lambda} z d \frac{dn}{d\lambda},$$

where z represents the thickness of the medium. HALLO'S investigations are concerned with the parts of the spectrum in the neighbourhood of an absorption band and for these we are justified in making the above supposition, as appears from a formula derived by VOIGT

¹⁾ FITZGERALD. Proc. Roy. Soc. 63 p. 31.

²⁾ HALLO. Diss. Amsterdam 1902, p. 7.

from a more rigorous theory¹⁾. If, however we want to apply it to points at a greater distance from an absorption band, as is the case with the magnetic rotation of transparent substances, we must turn to VOIGT's more general formula²⁾

$$n = 1 + \Sigma \frac{\epsilon_h \mathfrak{D}^2 (\mathfrak{D}^2 - \mathfrak{D}_h^0 \pm c_h R \mathfrak{D})}{(\mathfrak{D}^2 - \mathfrak{D}_h^0 \pm c_h R \mathfrak{D})^2 + \mathfrak{D}_h^2 \mathfrak{D}^2}$$

If we may assume that only one term occurs under the summation in the second member, and also that $c_h R$ and \mathfrak{D}_h^1 are small compared with \mathfrak{D} , a simple reduction shows that the new dispersion curve may be derived from the original one by moving each point over a distance $\frac{1}{2} c_h R \frac{\mathfrak{D}^2}{\mathfrak{D}_h^2}$, which depends on \mathfrak{D} and hence also on the wave-length. In this case HALLO's relation will hold, if σ is not supposed constant, but proportional to λ^2 .

Though it is uncertain whether for a given transparent substance we are entitled to accept the formula for n with only one term under the summation, we may investigate to what results this would lead. From the elementary theory of the ZEEMAN effect it follows that

$$T^1 - T = \frac{e}{m} \frac{HT^2}{4\pi},$$

whence for the displacement of the dispersion curve

$$\sigma = \lambda^1 - \lambda = \frac{e}{m} \frac{HT^2 V}{4\pi} = \frac{e}{m} \frac{H\lambda^2}{4\pi V}.$$

This value has been derived for the absorption band. From the above considerations it follows, however, that we may apply it for each wave-length, and hence we find

$$\omega = \frac{2\pi}{\lambda} z \frac{e}{m} H \frac{\lambda^2}{4\pi V} \frac{dn}{d\lambda} = z H \frac{e}{m} \frac{\lambda}{2V} \frac{dn}{d\lambda}.$$

Whence follows for the rotation constant $\varrho = \frac{\omega}{zH}$:

$$\varrho = \frac{e}{m} \cdot \frac{\lambda}{2V} \cdot \frac{dn}{d\lambda},$$

which formula corresponds with one, given by VOIGT³⁾, if we replace the k occurring there by:

$$k = \frac{e}{m} \cdot \frac{1}{2} V,$$

1) VOIGT. Wied. Ann. 67 p. 351.

2) VOIGT. Wied. Ann. 67 p. 349.

3) VOIGT. Wied. Ann. 67 p. 351.

which value may also be derived directly, if we equate the magnetic displacement $\frac{1}{2} c_h R$ after VOIGT with that resulting from the elementary theory. The dispersion of the magnetic rotation expressed by this formula is the same as that resulting from BECQUEREL'S ¹⁾ relation and found by him to be confirmed in the case of carbon disulphide and creosote.

The relation found for ϱ enables us to compute $\frac{e}{m}$ as soon as we know the rotation constant ϱ and the dispersion $\frac{dn}{d\lambda}$ of a substance for the same wavelength λ . For we have

$$\frac{e}{m} = \frac{2V}{\lambda} \varrho \frac{d\lambda}{dn}.$$

We shall make the calculation for some substances at a value of $\lambda = 589 \mu\mu$. The rotation constants r being usually expressed in minutes we have

$$\varrho = r \frac{2\pi}{360 \times 60}$$

and hence we find

$$\frac{e}{m} = \frac{2 \times 3 \times 10^{10}}{589} \frac{2\pi}{360 \times 60} \times r \frac{d\lambda}{dn} = 2.96 \times 10^4 \times r \frac{d\lambda}{dn}.$$

1. *Air* (100 KG., 13°.0). I have found ²⁾ $r = 553.10^{-6}$. PERREAU ³⁾ finds for the refractive index at (1 atm., 0° C.)

$$\begin{array}{r} \lambda = 644, \quad n - n_D = 85.10^{-8} \\ \quad \quad \quad 538 \quad \quad \quad 88.10^{-8} \end{array}$$

whence $\frac{d\lambda}{dn} = 0.65 \times 10^8$ and 0.58×10^8 , on an average 0.61×10^8 .

Supposing $n-1$ proportional to the density, it follows that for air (100 kilogram, 13°.0 C.) $d\lambda/dn = 0.648 \times 10^8$ and we find:

$$\frac{e}{m} = 2.96 \times 553 \times 0.648 \times 10^4 = 1.06 \times 10^7.$$

In the same way is found for:

2. *Carbon dioxide* (1 atm. 6°.5). $r = 8.62 \times 10^{-6}$

$$\frac{d\lambda}{dn} (1 \text{ atm., } 0^\circ) = 3.42 \times 10^7$$

$$(1 \text{ atm., } 6^\circ.5) = 3.50 \times 10^7$$

¹⁾ BECQUEREL. C. R. 125 p. 679.

²⁾ SIERTSEMA. Comm. Lab. Leiden. Suppl. N^o. 1, p. 86; Arch. Néerl. (2) 2 p. 376.

³⁾ PERREAU. Ann. de Ch. et de Ph. (7) 7 p. 289.

$$\frac{e}{m} = 0.89 \times 10^7.$$

3. *Hydrogen* (85.0 Kilogram, 9°.5 C.) $r = 456 \times 10^{-6}$
 $d\lambda/dn$ (1 atm., 0° C.) = 10^8
 (85.0 KG., 9°.5 C.) = 1.31×10^6 ,

$$\frac{e}{m} = 1.77 \times 10^7.$$

4. *Water*. From refractive indices of DUFET ¹⁾ and the magnetic rotation constant 0.0130 we get

$$\frac{e}{m} = 1.25 \times 10^7.$$

5. *Carbon disulphide*. In the same way with $r = 0.042$ we find from VAN DER WILLIGEN'S ²⁾ refractive indices

$$\frac{e}{m} = 0,745 \times 10^7.$$

6. *Quartz*. $r = 0.01684$ ³⁾. By means of VAN DER WILLIGEN'S refractive indices we find

$$\frac{e}{m} = 1.25 \times 10^7.$$

It may be remarked that the values of $\frac{e}{m}$ found here correspond in order of magnitude with those found in other ways.

¹⁾ DUFET. Bull. Soc. Minér. 8 p. 218.

²⁾ V. D. WILLIGEN. Arch. Mus. Teyler III. 1. p. 55.

³⁾ BOREL, C. R. 128, p. 1095.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday January 31, 1903.



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The following papers were read:

Chemistry. — "*The velocity of transformation of Carbon monoxide.*"

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

(Communicated in the meeting of December 27, 1902).

From the researches of BOUTOUARD¹⁾ on the equilibrium $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$, where use was made of the accelerating action of the metals Ni, Co, Fe, it follows that they do not modify the equilibrium but only

¹⁾ Ann. de Chimie et de Physique [7] 24, p. 5 (1901).

exercise an influence on the velocity and are, therefore, catalyzers. It was shown by BOUDOUARD that, whilst CO_2 in contact with C is practically totally converted at 1000° into CO, the amount of CO_2 in the gaseous mixture in equilibrium increases at lower temperatures in accordance with the sign of the heateffect $\text{CO}_2 + \text{C} = 2\text{CO} - 42000$ cal. until at 445° the CO is practically completely converted into CO_2 and C.

From this follows that below 445° , CO exists in a *metastable* condition.

INVESTIGATION.

a. Preparation of the catalyzer and preliminary experiments.

1. The following research was instituted with the object of determining velocities of reaction in the metastable region in presence of a catalyzer. The apparatus employed by us was in the main the same as that used by VAN 'T HOFF in his research on the velocity of transformation of detonating gas into water. The reaction vessel, however, was filled with a catalyzer obtained in the following manner.

Pumice stone was broken up into small lumps, drenched with a solution of $\text{Ni}(\text{NO}_3)_2$ then dried, ignited and finally reduced in a current of hydrogen or carbon monoxide.

This reduction, it was observed, takes place in two stages. The greyish-black surface of NiO first turns yellow owing to the formation of a suboxide ($\text{Ni}_2\text{O}^?$)¹⁾ and afterwards on complete reduction again becomes dark-grey. When operating at a high temperature, reduction with H_2 or CO gives apparently, the same material. If, however, the reduction takes place in a current of CO at 445° a layer of carbon is deposited on the reduced nickel.

2. The experiments with nickel-pumice obtained by reduction with either H_2 or CO at a *high* temperature gave the following result²⁾.

At 310° (boiling point of diphenylamine) the activity of the catalyzer did not appear constant. Successive fillings continually gave smaller diminutions of pressure in the same length of time.

1) MÜLLER, Bell (Chemical News 20, 258).

2) Coating the inner wall of the reaction vessel with nickel did not appear to affect the result, probably because the surface of the glass wall was very small as compared with the surface of the catalyzer.

We found for instance:

310°.

Filling.	Diminution in mM. Hg. during 10 minutes.
1st	5,68
2nd	5,00
3rd	3,80
	ect.

As we suspected that the retrogression of the activity of the catalyzer was due to the ever increasing layer of C, which deposits on the catalyzer during the experiment and fillings, we next used a nickel-pumice which had been reduced at 445° and was in consequence already coated with a layer of carbon. Although at first there was still a perceptible diminution in the activity, the differences in successive fillings become gradually smaller and finally, the activity was constant as seen from the following table:

310°

Filling.	Diminution in mM. Hg. during 10 minutes.
1st	1,88
2nd	1,80
3rd	1,78
4th	1,74
5th	1,75
6th	1,74
7th	1,74

Being satisfied with this result, we started our investigation with the catalyzer of constant activity obtained in this way.

b. Measurements concerning the order of the reaction.

For the determination of the order of the reaction the method of VAN 'T HOFF was first of all applied. It is given in this case by the equation:

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

The determination was made at 310°.

In the first experiment the pressure of the CO was 786,8 mm. Hg at the commencement; after 30 minutes the pressure amounted to 739,9 mm. Hg. The diminution of pressure in 30 minutes therefore amounted to 46,9 mm. Hg.

If we take for $\frac{dc}{dt}$ the diminution of pressure per minute then $\frac{dc_1}{dt}$ becomes 1,56.

In the second experiment the pressure of the CO was 535,3 mm. Hg at the commencement and after 30 minutes the pressure had come down to 501,7 mm. Hg. Here, the diminution of pressure in 30 minutes amounted, therefore, to 33,6 mm. Hg or $\frac{dc_2}{dt} = 1,12$.

C_1 = aver. of press. at beginn. and end at the 1st experim. = 763,35 mm. Hg.

C_2 = " " " " " " " " " " 2nd " = 518,5 " "

If from this we calculate n , we find

$$n = 0,86,$$

from which it is apparent that the reaction is a monomolecular one. In order to make more certain of this, the order of the reaction was also determined at two other temperatures according to the method given by NOYES. In this case n is calculated from the following formula:

$$n = 1 + \frac{\log \frac{t_1}{t_2}}{\log \frac{c_2}{c_1}}$$

in which t_1 and t_2 are the times during which the same part of the original quantity is converted when starting from different concentrations c_1 and c_2 .

At 256° we obtained the following result:

$$n = 1 + \frac{\log \frac{192}{200}}{\log \frac{525,1}{770,9}} = 1,1.$$

The experiment at 340° gave

$$n = 1 + \frac{\log \frac{60}{58}}{\log \frac{519,0}{792,8}} = 0,92.$$

The observations at the three temperatures 256°, 310° and 340°, therefore lead to the conclusion that we are really dealing here with a *monomolecular* reaction.

c. Determination of the reaction-constant at 256°, 310°, 340°.

These determinations were conducted with the same reaction vessel and the same catalyzer.

256° (boiling point of amyl benzoate).

Time in minutes.		Pressure in m.m. Hg	$k = \frac{1}{t} \log \frac{P_0}{2P_t - P_0}$
1	2		
0		761.0	—
5	0	758.9	0.000464
10		757.6	0.000381
	10	756.4	0.000287
	20	754.1	0.000276
	30	751.7	0.000277
	40	749.3	0.000278
average			0.000279

The following may serve to elucidate this table:

At 256° the catalyzer seemed to still perceptibly absorb the CO, which caused the diminution of pressure during the first 5 minutes to be excessive. The values for k are, therefore, not constant when we start from the pressure corresponding with the time 0, but they gradually diminish which may be seen from the first two figures in the last column of the table. To eliminate the error caused by absorption, we have, when calculating k , started from the pressure corresponding with the time 5 minutes (column 2) and, therefore, have called this pressure P_0 . As the CO concentration had diminished very little in 5 minutes the error thus introduced could be disregarded. The values obtained for k are found in the last column beneath the dotted line. The following table relates to the temperature 310°.

310° (boiling point of diphenylamine)

Time in minutes	Pressure in m.m. Hg	$k = \frac{1}{t} \log \frac{P_0}{2P_t - P_0}$
0	786.8	
10	769.8	0.00192
20	754.8	0.00184
30	739.9	0.00184
40	725.6	0.00184

average 0.00186

As was to be expected, the absorption at this high temperature was scarcely perceptible and in the following table, which shows the results obtained at 340°, no absorption whatever was noticed.

340° (boiling point of phenantrene)

Time in minutes	Pressure in m.m. Hg	$k = \frac{1}{t} \log \frac{P_0}{2P_t - P_0}$
0	791.4	
10	746.4	0.00524
20	705.9	0.00527
30	668.7	0.00536
50	612.7	0.00521

average 0.00527

In order to make sure that the activity of the catalyzer had not diminished during these three series, a series of experiments was finally taken at 310° with the following result.

310°

Time in minutes	Pressure in m.m. Hg	$k = \frac{1}{t} \log \frac{P_0}{2P_t - P_0}$
0	895.5	
10	788.3	0.00189
20	773.0	0.00183
30	757.8	0.00182
40	742.8	0.00184

average 0.00184

The activity of the catalyzer had, therefore, undergone no change during these measurements, so that we were justified in calculating the temperature-coefficient from the results obtained. The result was as follows:

Temperature.	k .	$\frac{k_{t+10}}{k_t}$
256°	0.000279	
310°	0.00186	>1,4
340°	0.00527	>1,4

d. Mechanism of the reaction.

What idea are we to form about the mechanism of the reaction if this takes a monomolecular course?

If we assume the formation of $\text{Ni}(\text{CO})_4$ with an immeasurably large velocity and the subsequent breaking up of this compound according to the equation



we must also accept the equilibrium



of which the constant is given by the equation:

$$K = \frac{C_{\text{CO}}^4}{C_{\text{Ni}(\text{CO})_4}}$$

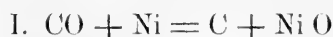
This would then necessarily lead to the conclusion, that the velocity

of reaction should be proportional to the 4th power of the CO-concentration whereas it appears to be proportional to the 1st power of the CO-concentration. Rejecting this hypothesis two further suppositions remain.

Firstly :



Secondly :



In the last case it need not be assumed that one of these reactions takes place with unmeasurable velocity, but only that the second one proceeds more rapidly than the first.

As regards the nature of the catalyzer we think we may conclude from the result of several experiments, that it is not the carbon but the finely divided nickel which possesses the catalytic action.

Amsterdam, Chem. Lab. University. Dec. 1902.

Chemistry. — Professor BAKHUIS ROOZEBOOM presents a communication from Dr. J. J. VAN LAAR on: “*The course of the melting-point-lines of solid alloys or amalgams.*” (First Communication). (Communicated in the meeting of December 27, 1902).

1. In the researches of VAN HETEREN¹⁾ on Tinamalgams a meltingpoint-line occurs²⁾ of a kind, which has not as yet been studied over such an extended course (from 0 to nearly 100 atom % of mercury). This is chiefly due to the fact, that the temperatures of fusion of the two metals are so very different; tin 231°, mercury —38.6°. In consequence the meltingpoint-line of the tin meets that of the mercury

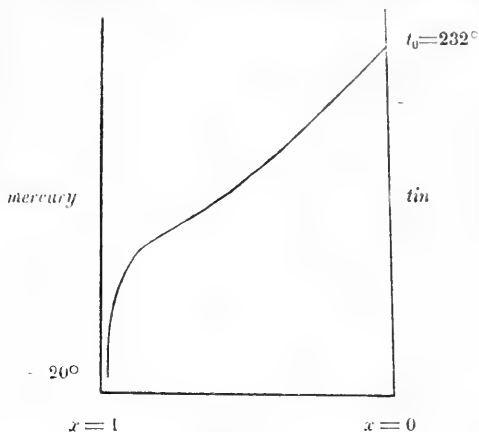


Fig. 1.

practically at 100 atom % mercury, so that the meltingpoint-line of the mercury has not even been observed. We therefore see for the first time a meltingpoint-line in its full course, and the question arises whether the course, found by VAN HETEREN, may be predicted theoretically.

The answer to this is in the affirmative. Let us, to start with, take the most simple view as regards the molecular poten-

¹⁾ Dissertation 1902. (also Report Meeting 29 Nov. 1902).

²⁾ l. c. pg. 18.

tials μ of the tin as solid substance and μ_1 of the tin in the liquid amalgam, namely that

$$\left. \begin{aligned} \mu &= e - c T \\ \mu_1 &= e_1 - c_1 T + RT \log(1-x) \end{aligned} \right\} \dots \dots \dots (1)$$

In this it has been assumed, firstly that the tin, crystallised from the amalgam, does not consist of mixed crystals, but of pure tin — a supposition, which has been proved by experiment to be nearly correct — and secondly, that the energy-quantity e is no function of x . Later on we will drop this last simplified supposition, and demonstrate, that a more accurate calculation of the function μ_1 affects the course of the meltingpoint-lines *quantitatively*, but not *qualitatively*. Then it is our object to demonstrate at once, that the entire qualitative course, as represented in the figure, follows from the equations (1) in connection with the *course of the logarithmic function of* $1-x$. By putting the two potentials equal to each other, we obtain:

$$(e_1 - e) - (c_1 - c) T = - RT \log(1-x),$$

or calling $e_1 - e = q$ (the heat of fusion of the solid tin, when passing into the amalgam), and the quantity $c_1 - c = \gamma$:

$$q - \gamma T = - RT \log(1-x),$$

from which follows:

$$T = \frac{q}{\gamma - R \log(1-x)} \dots \dots \dots (2)$$

This is then the most simple form of the meltingpoint-line.

On introducing the temperature of fusion of pure tin T_0 , x becomes 0, and we obtain:

$$T_0 = \frac{q}{\gamma},$$

so that we may also write:

$$T = \frac{T_0}{1 - \frac{RT_0}{q} \log(1-x)} = \frac{T_0}{1 - \theta \log(1-x)}, \dots \dots \dots (3)$$

if we abbreviate $\frac{RT_0}{q}$ to θ .

We notice at once, that on the development of the logarithmic function, the formula, for very small values of x , passes into

$$T = \frac{T_0}{1 + \frac{RT_0}{q} x},$$

that is to say into
$$T_0 - T = \frac{RT_0}{q} x,$$

the ordinary formula of VAN 'T HOFF for extremely dilute solutions. If, however, the solutions are no longer extremely dilute, we can no longer be satisfied with one or two terms in the development of $\log(1-x)$, but $\log(1-x)$ must remain.

I will now show, that the approximative relation

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

gives indeed the observed course qualitatively. For $\frac{dT}{dx}$ we find:

$$\frac{dT}{dx} = - \frac{T_0}{(1 - \theta \log(1-x))^2} \cdot \frac{\theta}{1-x}.$$

Whilst T itself, for $x=0$, passes into T_0 , and for $x=1$ into $T=0$, which already agrees with the steadily declining course — it appears from $\frac{dT}{dx}$, that this quantity, for $x=0$, becomes:

$$\left(\frac{dT}{dx}\right)_0 = - T_0 \theta = - \frac{RT_0^2}{q},$$

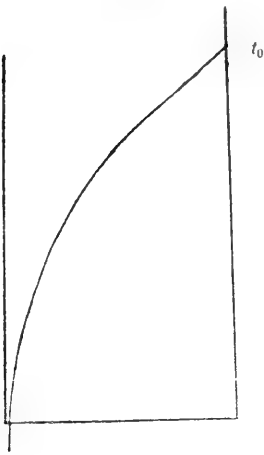


Fig. 2.

the limiting value of VAN 'T HOFF, whilst for $x=1$ it passes into $-\infty$. It may now still be asked, whether there will be a point of inflection or not. In the case, examined by VAN HETEREN, a point of inflection plainly occurred at about $x=0.8$, but it may also be possible, that the course was like the one in the following figure, without point of inflection. Let us therefore determine $\frac{d^2T}{dx^2}$.

$$\frac{d^2T}{dx^2} = \frac{2 T_0}{(1 - \theta \log(1-x))^3} \cdot \frac{\theta^2}{(1-x)^2} - \frac{T_0}{N^2} \cdot \frac{\theta}{(1-x)^2} = \frac{T_0}{N^2} \cdot \frac{\theta}{(1-x)^2} \left[\frac{2\theta}{N} - 1 \right].$$

Evidently $\frac{d^2T}{dx^2} = 0$, when $2\theta = N$, that is to say, when

$$\begin{aligned} 1 - \theta \log(1-x) &= 2\theta \\ -\log(1-x) &= 2 - \frac{1}{\theta}. \end{aligned}$$

As $\theta = \frac{RT_0}{q}$ will be positive, we see, that the point of inflection can

only occur if θ is situated between $1/2$ and ∞ . For $\theta = 1/2$, $x = 0$; for $\theta = \infty$ we find on the other hand $x = 0.865$. A point of inflection further than $x = 0.865$ can only occur with negative values for θ ($\theta = -\infty$ till $\theta = 0$, when $x = 0.865$ till $x = 1$). But there is no point of inflection if $\theta < 1/2$, that is to say, if

$$q > 2 R T_0,$$

or in gram-cals.

$$q > 4 T_0.$$

In our case therefore, where $T_0 = 505$ — when $q > 2000$ gram-cals.

This last conclusion will however be modified, when we apply the necessary correction to the approximate formula (3). *But the fact of the possible occurrence of a point of inflection* may already be completely explained by the simple formula (3), and this by the course of the function $\log (1-x)$.

II. We now proceed to write down a more stringent relation than (3).

Assuming an equation of condition of the VAN DER WAALS'S kind, the value of μ_1 (the molecular potential of the component n_1) becomes as follows:

$$\begin{aligned} \mu_1 = & -k_1 T (\log T - 1) - RT (\log (V-b) - 1) + \left((e_1)_0 - T (\eta_1)_0 \right) + \\ & + \frac{\sum n_i \cdot RT}{V-b} b_1 - \frac{2}{V} (n_1 a_{11} + n_2 a_{12} + \dots) + RT \log n_1 \quad \dots \quad (4) \end{aligned}$$

For b has been written:

$$b = n_1 b_1 + n_2 b_2 + \dots,$$

whilst for a the quadratic relation

$$a = n_1^2 a_{11} + 2 n_1 n_2 a_{12} + \dots$$

has been taken.

Now, $\log (V-b)$ can be supposed to be independent of x , whilst the expression

$$\frac{\sum n_i \cdot R T}{V-b} b_1 - \frac{2}{V} (n_1 a_{11} + n_2 a_{12}) = \frac{RT}{V-b} b_1 - \frac{2}{V} ((1-x)a_{11} + x a_{12})$$

in regard to x will become not of the order x , but of x^2 . Let us, to prove this, rather start from a more general expression for the total potential ζ (in our case we have only to deal with two single components n_1 and n_2), namely

$$\begin{aligned} \zeta = & n_1 (\mu_1)_0 + n_2 (\mu_2)_0 + \frac{n_1^2 \mu_{11} + 2 n_1 n_2 \mu_{12} + n_2^2 \mu_{22}}{n_1 + n_2} + \\ & + RT \left(n_1 \log \frac{n_1}{n_1 + n_2} + n_2 \log \frac{n_2}{n_1 + n_2} \right). \end{aligned}$$

We then find:

$$\mu_1 = \frac{\partial \xi}{\partial n_1} = (\mu_1)_0 - \frac{1}{(n_1 + n_2)^2} (n_1^2 \mu_{11} + 2 n_1 n_2 \mu_{12} + n_2^2 \mu_{22}) + \frac{2}{n_1 + n_2} (n_1 \mu_{11} + n_2 \mu_{12}) + RT \log \frac{n_1}{n_1 + n_2}.$$

With $n_1 + n_2 = 1$, $n_1 = 1-x$, $n_2 = x$ we obtain:

$$\mu_1 = (\mu_1)_0 - [(1-x)^2 \mu_{11} + 2x(1-x)\mu_{12} + x^2 \mu_{22}] + 2[(1-x)\mu_{11} + x\mu_{12}] + RT \log(1-x),$$

or after simplification:

$$\mu_1 = [(\mu_1)_0 + \mu_{11}] - x^2 (\mu_{11} - 2 \mu_{12} + \mu_{22}) + RT \log (1 - x).$$

In analogy with (4) we may therefore write:

$$\mu_1 = e_1 - c_1 T + \alpha_1 x^2 + RT \log (1-x).$$

The terms with $T \log T$ have not been taken into consideration, because they disappear on account of the equality of the quantities k_1 and R in the liquid and in the solid phase.

If, for the sake of a closer approximation, we take up some higher powers of x , we finally get:

$$\left. \begin{array}{l} \text{(solid tin)} \quad \mu = e - cT \\ \text{(tin in liquid amalg.)} \quad \mu_1 = e_1 - c_1 T + (\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4) + RT \log(1-x) \end{array} \right\} \quad (5)$$

Equating, we then find as in § 1:

$$q_0 - \gamma T = - (\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4) - RT \log (1-x),$$

or

$$T = \frac{q_0 + (\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4)}{\gamma - R \log(1-x)} \dots \dots \dots (6)$$

The heat of fusion of the solid tin in the amalgam is now plainly:

$$\underline{q = q_0 + (\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4)} \dots \dots \dots (7)$$

For $x = 0$, (6) passes into

$$T_0 = \frac{q_0}{\gamma},$$

so we may again write:

$$T - T_0 = \frac{1 + \frac{\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4}{q_0}}{1 - \frac{RT_0}{q_0} \log(1-x)},$$

or with $\frac{\alpha_1}{q_0} = \alpha$, $\frac{\beta_1}{q_0} = \beta$, $\frac{\gamma_1}{q_0} = \gamma$:

$$\underline{T = T_0 \frac{1 + (\alpha x^2 + \beta x^3 + \gamma x^4)}{1 - \theta \log(1-x)}}, \dots \dots \dots (8)$$

and this is the more accurate formula, which has taken the place of the simple relation (3).

III. We will now show, that the above formula quantitatively yields the values, found by VAN HETEREN for T , in a satisfactory manner.

As $-\left(\frac{dT}{dx}\right)_0 = T_0 \theta$, θ may be determined with great accuracy from the beginning course of the meltingpoint-line. From the values, found for T (on pg. 16 of the dissertation) for $x = 0$ atom % of mercury (pure tin), $x = 0,1005$, $x = 0,1716$ and $x = 0,2338$, the average value, obtained for $-\frac{dT}{dx}$ is $= 200$. From the determinations of HEYCOCK and NEVILLE between $x = 0$ and $x = 0,1$ it also follows, that $-\frac{dT}{dx} = 200$. For θ we may therefore take ($T_0 = 505$):

$$\theta = \frac{200}{505} = \underline{0,4}.$$

I calculated the values of α , β and γ as follows:

$$\underline{\alpha = 0,325} \quad ; \quad \underline{\beta = -1,11} \quad ; \quad \underline{\gamma = 1,33}.$$

Formula (8) thus becomes:

$$T = T_0 \frac{1 + (0,325x^2 - 1,11x^3 + 1,33x^4)}{1 - 0,4 \log(1-x)},$$

and so we find the following values for T .

The agreement is as good as can be expected: the difference between the calculated value of T and the observed value generally amounts to fractions of a degree, average $0,8$; as regards to the absolute temperatures the deviation is only average $0,2\%$. Only the two last values are too low (the last 3%), but then the influence of a small inaccuracy in the determination of the coefficients β and γ makes itself strongly felt. If we except these two last values, the calculated meltingpoint-line fully coincides with the observed line in the scale of the figure in the dissertation. And by means of a slight alteration in the value of β and γ we might perhaps cause the two last observations to agree. Let us not forget, that the formula (8) always remains an approximate one. In the last values of x the composition of the separated tin must also make its influence felt. For this is no longer pure tin but contains certainly 1% , or perhaps even 6% of mercury.

As regards the value of q (the heat of fusion of tin, when passing into the amalgam) — when $x = 0$, $q = q_0$, that is to say $= \frac{RT_0}{\theta} = \frac{1010}{0,4} = 2550$ gram-cals. At 25° our formula is no longer available, as

x	x^2	x^3	x^4	$-\log(1-x)$	Numer.	Denom.	$T-273$ calcul.	$T-273$ found	Δ
0,1005	0,0101 ⁰	0,00101 ⁵	0,0001 ⁰²	0,1059	1,0023	1,0424	212,4	211,6	0,8
0,1716	0,0294 ⁵	0,0050 ⁵³	0,0008 ⁶⁷³	0,1883	1,0051	1,0753	198,9	198,6	0,3
0,2338	0,0546 ⁶	0,0127 ⁸	0,0029 ⁸⁸	0,2663	1,0076	1,1065	186,7	183,7?	3,0?
0,2969	0,0881 ⁵	0,0261 ⁷	0,0077 ^{7⁰}	0,3523	1,0099	1,1409	173,8	173,0	0,8
0,3856	0,1487	0,0573 ³	0,0221 ¹	0,4872	1,0141	1,1949	155,4	155,2	0,2
0,5001	0,2501	0,1251	0,0625 ⁵	0,6933	1,0256	1,2773	132,3	133,4	-1,1
0,5973	0,3568	0,2131	0,1273	0,9095	1,0488	1,3638	115,2	115,2	0,0
0,6467	0,4182	0,2705	0,1749	1,0404	1,0682	1,4161	107,7	107,4	0,3
0,6754	0,4562	0,3081	0,2081	1,1252	1,0830	1,4501	104,0	103,4	0,6
0,6813	0,4642	0,3162	0,2155	1,1435	1,0866	1,4574	103,3	102,4	0,9
0,7104	0,5047	0,3585	0,2547	1,2393	1,1047	1,4957	99,8	99,0	0,8
0,7155	0,5119	0,3663	0,2620	1,2570	1,1083	1,5028	99,2	98,8	0,4
0,7477	0,5591	0,4180	0,3126	1,3772	1,1335	1,5509	95,9	95,4	-0,5
0,7547	0,5696	0,4299	0,3244	1,4053	1,1393	1,5621	95,1	94,0	1,1
0,7963	0,6341	0,5049	0,4021	1,5912	1,1805	1,6365	91,1	90,0	1,1
0,8189	0,6706	0,5492	0,4497	1,7087	1,2064	1,6835	88,7	88,4	0,3
0,8921	0,7958	0,7100	0,6333	2,2266	1,3128	1,8906	77,5	79,7	-2,2
0,9483	0,8993	0,8528	0,8087	2,9623	1,4212	2,1849	55,3	65,2	-9,9

according to the above table it only yields trustworthy values for T up to about 90° . At 90° $x = 0,8$, and then, according to (7), we have:

$$q = q_0 [1 + (\alpha x^2 + \beta x^3 + \gamma x^4)],$$

or

$$q = q_0 [1 + 0,325 x^2 - 1,11 x^3 + 1,33 x^4],$$

that is to say $q = 1,185 q_0 = 3020$ gram-cals.,

whilst VAN HETEREN (at 25°) found ± 3000 gram calcs, by means of electromotive measurements¹⁾. The concordance is absolute.

We, finally, wish to remark, that according to the determinations of VAN HETEREN and of HEYCOCK and NEVILLE, regarding the lowering of the temperature of fusion of tin on adding small quantities of mercury, q_0 must be $= 2550$ calcs. We therefore see, that the value, assigned by PERSON, namely $14,25 \times 118,5 = 1690$ gram calcs., is much too small. In a later communication I will show, that the heat of fusion of mercury, given by PERSON, is also many times too small.

Dec. 1902.

¹⁾ Dissertation pg. 49.

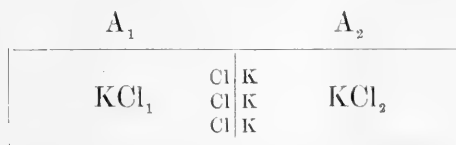
Chemistry. — “On the potential-difference, which occurs at the surface of contact of two different non-miscible liquids, in which a dissolved electrolyte has distributed itself.” By Dr. J. J. VAN LAAR. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM.)

(Communicated in the meeting of December 27, 1902.)

1. It has already been demonstrated by NERNST¹⁾ in 1892, that a potential-difference must occur at the surface of contact of two liquids, which lie together in layers, such as for instance water and phenol, on account of the unequal distribution of the neutral molecules and the Ions of a dissolved electrolyte. It is true, that his expression for the electromotive force relates to the case, that one of the two phases is a *solid* solution, but it will be perceived at once, that the same formula also applies to our case²⁾.

There is, however, at present no prospect of obtaining direct measurements of this potential-difference³⁾. But as RIESENFELD⁴⁾ has lately been experimenting on the subject, although in another direction, it may be as well to give the exact theory of the phenomenon, which I worked out about a year ago, when engaged in writing a book on electro-chemistry, which will be published later.

Suppose we have a solution of KCl in the solvents A_1 and A_2 ,



If now equilibrium has been established between the *non-dissociated*, electrically neutral portions of the dissolved KCl in the two phases, there need not be equilibrium between the *Ions* in the two solvents. Indeed, equating the thermodynamic potentials for equivalent quantities of the non-dissociated portions in the two phases (*equilibrium of partition*), we get:

$$\mu_{KCl_1} = \mu_{KCl_2} \quad \dots \quad (1)$$

But the two dissociation-equilibria give:

$$\mu_{KCl_1} = \mu_{K_1} + \mu_{Cl_1} \quad ; \quad \mu_{KCl_2} = \mu_{K_2} + \mu_{Cl_2} \quad \dots \quad (2)$$

Consequently it will suffice if

$$\mu_{K_1} + \mu_{Cl_1} = \mu_{K_2} + \mu_{Cl_2}, \quad \dots \quad (3)$$

¹⁾ Zeitschr. für Physik. Chemie **9**, 137 (1892).

²⁾ Compare RIESENFELD, Wied. Ann. (4) **8**, 617 (1902).

³⁾ Ibid., l. c.

⁴⁾ NERNST und RIESENFELD, l. c. p. 600—608; RIESENFELD, 609—615; 616—624; id. Inaug. Diss., Göttingen 1901; HITTORF, Wied. Ann. (4) **9**, 243—245 (1902).

and it would be a sheer accident if we also had:

$$\mu_{K_1} = \mu_{K_2} \quad ; \quad \mu_{Cl_1} = \mu_{Cl_2}$$

There exists therefore as a rule *no* equilibrium of partition between the *Ions* in the two solvents. For example there may be in the second solvent relatively too few K-Ions, too many Cl-Ions. Since a system out of equilibrium tends to pass into a condition of equilibrium, K-Ions from A_1 will migrate to A_2 , and remain there in the boundary-layer, while the corresponding liberated Cl-Ions remain in the boundary-layer of A_1 (inversely Cl-Ions will migrate from A_2 to A_1 , whilst the corresponding liberated K-Ions remain in A_2 . Both add themselves to the above mentioned similar ions in the boundary-layer). The consequence is the occurrence of an *electrical doublelayer* and therefore of a potential-difference. And it is this potential-difference, which will restore the originally non-existing equilibrium between the Ions.

All this may be put into a very simple mathematical form.

Let V_1 be the electrical potential of A_1 , V_2 that of A_2 , so that $\Delta = V_2 - V_1$ represents the potential-difference at the boundary (in the case we are dealing with, Δ is therefore *positive*), then the formula for the equilibrium of the K-Ions will be:

$$\frac{\mu_{K_2} - \mu_{K_1}}{\varepsilon} de + \Delta de = 0,$$

which is at once obvious, when we consider the virtual passage from the left to the right over the boundary of such a quantity of K-Ions, that the quantity of electricity transported is de . As the quantities μ relate to *equivalent*-quantities, and as these do not correspond with one electric unit, but with ε ($= 96530$) electric units, $\mu_{K_2} - \mu_{K_1}$ must be divided by ε .

For the equilibrium of the Cl-Ions we find in the same manner:

$$\frac{\mu_{Cl_2} - \mu_{Cl_1}}{\varepsilon} - \Delta de = 0.$$

The sign at Δ is now negative, because on account of the negative charge the change in the electrical energy is $-\Delta de$.

We therefore obtain from the two relations, after dividing by de :

$$\Delta = - \frac{\mu_{K_2} - \mu_{K_1}}{\varepsilon} = \frac{\mu_{Cl_2} - \mu_{Cl_1}}{\varepsilon} (4)$$

That these two equations for Δ are not conflicting, is at once apparent. For the relation, resulting therefrom

$$\mu_{K_1} - \mu_{K_2} = \mu_{Cl_2} - \mu_{Cl_1},$$

leads at once to (3).

If we introduce :

$$\mu = \mu' + RT \log c,$$

in which c is the concentration of the Ions, we may also write :

$$\left. \begin{aligned} \Delta &= -\frac{1}{\varepsilon} \left[(\mu'_{K_2} - \mu'_{K_1}) + RT \log \frac{c_{K_2}}{c_{K_1}} \right] \\ \Delta &= \frac{1}{\varepsilon} \left[(\mu'_{Cl_2} - \mu'_{Cl_1}) + RT \log \frac{c_{Cl_2}}{c_{Cl_1}} \right] \end{aligned} \right\} \dots \dots (5)$$

II. Now everywhere $c_K = c_{Cl}$ (only in the boundary-layer an excess of positive or negative Ions is present, owing to the formation of the doublelayer), therefore also

$$\frac{c_{K_2}}{c_{K_1}} = \frac{c_{Cl_2}}{c_{Cl_1}},$$

and so we find ¹⁾ by addition of the two equations (5) :

$$\Delta = \frac{1}{2\varepsilon} \left[(\mu'_{Cl_2} - \mu'_{Cl_1}) - (\mu'_{K_2} - \mu'_{K_1}) \right] \dots \dots (6)$$

From this last relation it follows at once, that in *dilute* solutions, where the quantities μ' are almost independent of the concentration, the potential-difference Δ will be also independent of the concentration. Whether *much* or *little* KCl is distributed through the two solvents, we will always notice about the *same* potential-difference Δ .

If we deduct the two equations from each other instead of adding,

then we obtain (observing that $\frac{c_{K_2}}{c_{K_1}} = \frac{c_{Cl_2}}{c_{Cl_1}}$):

$$RT \log \frac{c_{K_2}}{c_{K_1}} = -\frac{1}{2} \left[(\mu'_{Cl_2} - \mu'_{Cl_1}) + (\mu'_{K_2} - \mu'_{K_1}) \right] \dots \dots (7)$$

If now we put

$$\left. \begin{aligned} \mu'_{K_2} - \mu'_{K_1} &= RT \log K_K \\ \mu'_{Cl_2} - \mu'_{Cl_1} &= RT \log K_{Cl} \end{aligned} \right\} \dots \dots (a)$$

in which K_K and K_{Cl} are quantities, which depend on the nature of the two solvents (and which in *dilute* solutions will only be functions of *temperature*) — they are the so-called *partition-coefficients* of the positive and negative Ions — then (6) and (7) pass into

$$\Delta = \frac{RT}{2\varepsilon} \log \frac{K_{Cl}}{K_K} \dots \dots (6a)$$

$$\underline{\left(\frac{c_{K_1}}{c_{K_2}} \right)^2} = K_K \times K_{Cl} \dots \dots (7a)$$

¹⁾ The formula (6) was given already, though with a somewhat different notation, by LUTHER [Z. f. Ph. Ch. **19**, 537 (1896)]. The first thermodynamic theory of the equilibrium of partition was given by me in a paper of 1895 (Z. f. Ph. Ch. **18**, 264—267).

NERNST's formula for Δ , obtained in a different manner, is identical with our formula (5). (As NERNST's $E = V_1 - V_2$, our $\Delta = -E$). For if we replace $\mu'_{K_2} - \mu'_{K_1}$ by $RT \log K_K$ and $\mu'_{Cl_2} - \mu'_{Cl_1}$ by $RT \log K_{Cl}$, then (5) passes into

$$\Delta = -\frac{RT}{\varepsilon} \log K_K \frac{c_{K_2}}{c_{K_1}} = \frac{RT}{\varepsilon} \log K_{Cl} \frac{c_{Cl_2}}{c_{Cl_1}},$$

and this is NERNST's expression. As has already been observed, the quantities K_K and K_{Cl} are the so-called "partition-coefficients" of the positive and negative Ions. For instance for the positive Ions we should have, when equilibrium of partition occurs:

$$\mu_{K_2} - \mu_{K_1} = 0,$$

or

$$\mu'_{K_2} - \mu'_{K_1} + RT \log \frac{c_{K_2}}{c_{K_1}} = 0,$$

so that we obtain $\frac{c_{K_1}}{c_{K_2}} = K_K$. The same for the negative Ions.

The relation, given by NERNST¹⁾

$$K_K \times K_{Cl} = \frac{C_1}{C_2} \times K_{KCl},$$

in which K_{KCl} is the coefficient of partition of the neutral KCl-molecules, and C_1 and C_2 are the *dissociation* constants in the two phases, follows directly from the thermodynamical meaning of these quantities. For if we write this relation in the form

$$RT [\log K_K + \log K_{Cl}] = RT [\log C_1 - \log C_2 + \log K_{KCl}],$$

it passes, taking into account equation (a) and the relations

$$RT \log K_{KCl} = \mu'_{KCl_2} - \mu'_{KCl_1}; \quad RT \log C_1 = \mu'_{KCl_1} - \mu'_{K_1} - \mu'_{Cl_1};$$

$$RT \log C_2 = \mu'_{KCl_2} - \mu'_{K_2} - \mu'_{Cl_2},$$

immediately into the identity

$$\begin{aligned} (\mu'_{K_2} - \mu'_{K_1}) + (\mu'_{Cl_2} - \mu'_{Cl_1}) &= (\mu'_{KCl_1} - \mu'_{K_1} - \mu'_{Cl_1}) - \\ &- (\mu'_{KCl_2} - \mu'_{K_2} - \mu'_{Cl_2}) + (\mu'_{KCl_2} - \mu'_{KCl_1}). \end{aligned}$$

Not the formula (5), but the formula (6) or (6a), derived by us from (5), deserves however the preference, because the concentrations of the Ions have been eliminated therein, and an expression has been obtained, in which only the coefficients of partition K_K and K_{Cl} occur.

III. If the dissolved electrolyte has now distributed itself so, that

¹⁾ Z. f. Ph. Ch. 8, 138 (1891).

the total concentration is c_1 in A_1 and c_2 in A_2 , we shall have:

$$c_{K_1} = \alpha_1 c_1 \quad ; \quad c_{K_2} = \alpha_2 c_2,$$

in which the quantities c_1 and c_2 may be found by chemical analysis, and α_1 and α_2 by determinations of the conductivity. As soon as Δ can be determined by experiment, $\frac{K_{Cl}}{K_K}$ may be calculated from the equation (6a), and $K_K \times K_{Cl}$ from (7a), and we can therefore get to know separately the quantities K_K and K_{Cl} , consequently also the quantities

$$\mu'_{K_2} - \mu'_{K_1} \quad \text{and} \quad \mu'_{Cl_2} - \mu'_{Cl_1}.$$

From (6a) it further follows, that Δ will be *positive* (as supposed in the figure), when

$$K_{Cl} > K_K.$$

Only when by accident $K_{Cl} = K_K$, Δ can be 0. *In general a potential difference will always occur between two non-miscible solvents, when an electrolyte is partitioned between them.* This potential-difference is given by (6a).

From the equation (7a) it follows, that the relation of the concentrations of the *Ions* in the two solvents in the case of *dilute* solutions will be practically independent of the total concentrations. This equation may also be deduced directly from (3). For this, being a result of (1) and (2), that is to say of the equilibrium of partition and the two equilibria of dissociation, may be written:

$$(\mu'_{K_2} - \mu'_{K_1}) + (\mu'_{Cl_2} - \mu'_{Cl_1}) = -RT \left[\log \frac{c_{K_2}}{c_{K_1}} + \log \frac{c_{Cl_2}}{c_{Cl_1}} \right],$$

and this after substitution passes at once into (7a). For

$$\log \frac{c_{K_2}}{c_{K_1}} + \log \frac{c_{Cl_2}}{c_{Cl_1}} = 2 \log \frac{c_{K_2}}{c_{K_1}} = - \log \left(\frac{c_{K_1}}{c_{K_2}} \right)^2.$$

The equations (6a) and (7a) moreover lead to an important conclusion.

As the quantities K_K and K_{Cl} are, in the case of *dilute* solutions, *specific* quantities, we must therefore find about the *same values* for these quantities in the case of *other* salts, when employing the same solvents A_1 and A_2 . For NaCl for instance we will have:

$$\Delta' = \frac{RT}{2\varepsilon} \log \frac{K_{Cl}}{K_{Na}}; \quad \left(\frac{c_{Na_1}}{c_{Na_2}} \right)^2 = K_{Na} \times K_{Cl},$$

from which by experimental determination of Δ' and the quantities c_{Na_1} and c_{Na_2} , the two quantities K_{Na} and K_{Cl} may be determined. The value, found for K_{Cl} from KCl-solutions in A_1 and A_2 , must then be practically *identical* with the value for K_{Cl} , determined from solutions of NaCl in these solvents.

The quantities Δ will show an almost complete additive character, on account of K_K and K_{Cl} being independent of the concentration in the case of dilute solutions. For instance, in the same solvents A_1 and A_2 we must find:

$$\Delta_{KCl} - \Delta_{NaCl} = \Delta_{KNO_3} - \Delta_{NaNO_3}.$$

And the same for other combinations.

The above considerations may be readily extended to the case of *non-binary* electrolytes such as $CaCl_2$, $ZnCl_2$, etc. In the different equations the valencies ν of the Ions will then also occur, because the fundamental relation (4) then passes into the more general one:

$$\Delta = - \frac{\overset{+}{\mu_2} - \overset{+}{\mu_1}}{\overset{+}{\nu\epsilon}} = \frac{\overset{-}{\mu_2} - \overset{-}{\mu_1}}{\overset{-}{\nu\epsilon}}.$$

IV. The question in how far and in what manner the value of Δ , given in (6) or (6a), is still dependent on the concentrations of the Ions, can only be answered, when we calculate the values of μ'_{K_1} etc. with the aid of an equation of condition. If we accept the equation of VAN DER WAALS as also applying to liquid-phases, we obtain for instance for the molecules n_p :

$$\begin{aligned} \mu_p = & -k_p T (\log T - 1) - RT \left(\log \frac{V-b}{n_1} - 1 \right) + [(e_p)_0 - T(\eta_p)_0] + \\ & + RT \frac{\sum n_1}{V-b} b_p - \frac{2}{V} (n_1 a_{p1} + n_2 a_{p2} + \dots) + RT \log \frac{n_p}{n_1}. \end{aligned}$$

n_1 stands here for the molecular number of the solvent. For b and a we write:

$$\begin{aligned} b &= n_1 b_1 + n_2 b_2 + \dots \\ a &= n_1^2 a_{11} + 2 n_1 n_2 a_{12} + 2 n_1 n_3 a_{13} + \dots \end{aligned}$$

Let us now calculate the value of

$$(\mu'_{Cl_2} - \mu'_{Cl_1}) - (\mu'_{K_2} - \mu'_{K_1}),$$

or, what amounts to the same, of

$$(\mu'_{K_1} - \mu'_{Cl_1}) - (\mu'_{K_2} - \mu'_{Cl_2}).$$

If we indicate the solvent by the index 1, the non-dissociated KCl, dissolved therein, by 2, the two Ions by 3 and 4, we obtain for $\mu'_{K_1} - \mu'_{Cl_1}$ the expression

$$\begin{aligned} & - (k_3 - k_4) T (\log T - 1) + [(e_3)_0 - (e_4)_0 - T((\eta_3)_0 - (\eta_4)_0)] + \\ & + RT \frac{\sum n_1}{V-b} (b_3 - b_4) - \frac{2}{V} [n_1 (a_{31} - a_{41}) + n_2 (a_{32} - a_{42}) + n_3 (a_{33} - a_{43}) + n_4 (a_{34} - a_{44})]. \end{aligned}$$

Remembering, that $n_3 = n_4$, $a_{34} = a_{43}$, the last term may be simplified to

$$-\frac{2}{V} [n_1 (a_{31} - a_{41}) + n_2 (a_{32} - a_{42}) + n_3 (a_{33} - a_{44})].$$

For $\mu'_{K_2} - \mu'_{Cl_2}$ we find a similar expression. In this, however, the quantities k_3, k_4 (the heat-capacities of the same Ions, at infinite volume) and $(e_3)_0, (e_4)_0, (\eta_3)_0, (\eta_4)_0$ (the energy and entropy-constants of these Ions) will be exactly the same. a_{32}, a_{42}, a_{33} and a_{44} will also remain unaltered, so that for the difference $(\mu'_{K_1} - \mu'_{Cl_1}) - (\mu'_{K_2} - \mu'_{Cl_2})$ we may write:

$$RT \left[\frac{\sum n_1}{V-b} (b_3 - b_4) - \frac{\sum n'_1}{V'-b'} (b'_3 - b'_4) \right] - 2 \left[\left(\frac{n_1 (a_{31} - a_{41})}{V} - \frac{n'_1 (a'_{31} - a'_{41})}{V'} \right) + (a_{32} - a_{42}) \left(\frac{n_2}{V} - \frac{n'_2}{V'} \right) + (a_{33} - a_{44}) \left(\frac{n_3}{V} - \frac{n'_3}{V'} \right) \right].$$

The quantities, relating to the second solvent, are indicated by accents.

We may now go a step further and accept as a first approximation:

$$b_3 = b_4, b'_3 = b'_4, a_{32} = a_{44}.$$

If we then also write

$$\frac{V}{n_1} = v, \frac{V'}{n'_1} = v', n_2 = n(1-\alpha), \frac{n}{n_1} = c, \text{ etc.,}$$

we finally obtain for Δ :

$$\Delta = \frac{1}{\varepsilon} \left[\left(\frac{a'_{31} - a'_{41}}{v'} - \frac{a_{31} - a_{41}}{v} \right) + (a_{32} - a_{42}) \left(\frac{(1-\alpha)c'}{v'} - \frac{(1-\alpha)c}{v} \right) \right]. \quad (6b)$$

As, in consequence of the equilibrium of partition, $\frac{(1-\alpha)c'}{(1-\alpha)c}$ is constant, Δ will have the form

$$\Delta = \Delta_0 + \lambda (1-\alpha)c,$$

or since, on account of the equilibrium of dissociation, $\frac{(ac)^2}{(1-\alpha)c} =$ constant, also the form

$$\Delta = \Delta_0 + \lambda' (\alpha c)^2.$$

Whether Δ will be positive or negative, depends chiefly on Δ_0 . If

$$\frac{a_{31} - a_{41}}{v} < \frac{a'_{31} - a'_{41}}{v'},$$

Δ will be positive. We also see, that $\Delta - \Delta_0$ will increase or decrease with the *second* power of αc , that is to say in the case of strongly dissociated electrolytes, where α is nearly 1, almost with c^2 .

Dec. 1902.

Physics. — Dr. J. J. HALLO: “*The value of some magneto-optic constants.*” (Communicated by Prof. P. ZEEMAN).

In my doctoral thesis, on *The magnetic rotation of the plane of polarisation in the neighbourhood of an absorption-band*¹⁾, I have calculated the values which three of the constants, occurring in VOIGT'S theory of magneto-optic phenomena, assume in a particular case. I did not then know as yet, that DRUDE had already tried — in his *Lehrbuch der Optik* (Leipzig, 1900) — to make some estimate as to the order of magnitude of a constant r , introduced by him, which is connected in a simple manner with one of the constants of VOIGT'S theory, of which I have determined the value. Therefore I beg to be allowed to mention here my results and those of DRUDE, and to examine in how far these results agree.

If \mathfrak{X} , \mathfrak{Y} , \mathfrak{Z} are the components of the electric polarisation in some medium, VOIGT assumes that every one of these components exists of a part X , Y , Z , relating to the free ether, and a series of other parts \mathfrak{X}_h , \mathfrak{Y}_h , \mathfrak{Z}_h , indicating the state of the ponderable matter. He therefore assumes:

$$\mathfrak{X} = X + \sum \mathfrak{X}_h, \text{ etc.}$$

A representation of the phenomena of selective absorption, in which the influence of a magnetic field with components A , B , C is also taken into account, is gained when the sets of vector-components A , B , C are subjected to the conditions:

$$\mathfrak{X}_h + a_h \frac{\partial \mathfrak{X}_h}{\partial t} + b_h \frac{\partial^2 \mathfrak{X}_h}{\partial t^2} + c_h \left(C \frac{\partial \mathfrak{Y}_h}{\partial t} - B \frac{\partial \mathfrak{Z}_h}{\partial t} \right) = \varepsilon_h X, \text{ etc.}$$

The constant b_h appears to be equal to $\tau_h^2/4\pi^2$, if τ_h is the vibratory period of a free vibration of the absorbing medium; I have derived the values of the constants a_h , c_h and ε_h for the line D_2 from the results of my measurements in a particular case (for a flame which contained very much sodium); the values I have found are (*vide* p. 85 of my thesis):

$$a_h = 1 \cdot 10^{-20};$$

$$c_h = 0,2 \cdot 10^{-23};$$

$$\varepsilon_h = 7,5 \cdot 10^{-8}.$$

The constants a_h and ε_h depend on the density of the sodium-vapour in the flame, the constant c_h does not so far as we know.

The data which served for the calculation of these constants are the following: a_h was calculated from the width of the absorption-

¹⁾ Amsterdam, 1902.

band, which is proportional to it; this width was about 1 Angström Unit; c_h was calculated from the magnitude of the ZEEMAN-effect; for this magnitude in the field which I used — of 9000 C. G. S. Units — I took $\frac{1}{20}$ part of the interval between the two sodium-lines; ϵ_h was calculated from the value of the rotation of the plane of polarisation in the neighbourhood of the absorption-band; on the magnitude of this rotation as a function of the wavelength, for different intensities of the magnetic field and different widths of the absorption-bands, I have made measurements of which the results have been recorded in the tables given in my thesis. From these tables I shall quote one series here, giving the numbers from which the above-mentioned value of ϵ_h was deduced (*vide* p. 42 of my thesis, table 24 I):

δ	χ	δ	χ
15	88	50	11
20	51	55	10
25	31	60	9
30	23	65	8
35	18	70	6
40	14	75	5
45	12		

Here δ is proportional to the difference between the wavelength of a given kind of light and the wavelength which corresponds with the middle of the line D_2 ; the coefficient of proportion may be found from the fact that the difference between the wavelengths of the two sodiumlines corresponds with a value $\delta = 130$; χ represents the rotation of that particular kind of light in my experiments, expressed in a unit of which the value is determined by the fact that a rotation of 180° corresponds with a value $\chi = 105$. Thus we read from the series, given above, that for a value of δ corresponding with $\frac{35}{130} \times 6$ A. U. the rotation of the plane of polarisation is $\frac{18}{105} \times 180^\circ$; from these corresponding numbers the value of ϵ_h is deduced in the way which I explained in my thesis.

DRUDE, in his *Lehrbuch der Optik* which I mentioned above (p. 353), in his version of the theory of dispersion gives the equations of motion of an electron in the form:

$$m \frac{\partial^2 \xi}{\partial t^2} = eX - \frac{4\pi e^2}{\mathfrak{D}} \xi - r e^2 \frac{\partial \xi}{\partial t}.$$

Here m is the mass, e the charge of the electron, ξ its displacement parallel to the axis of X from a position of equilibrium, X the component parallel to this axis of the external electric force acting on the electron; r and \mathfrak{D} are positive constants.

In working out the theory it appears that VOIGT's constant a_h is identical with the expression $r\mathfrak{D}/4\pi$ of DRUDE. Now the value of \mathfrak{D} was calculated by DRUDE himself (p. 490) from the vibratory period of the sodiumlines; he finds the value of this constant to be $7,6 \cdot 10^{-23}$; from this value and that of VOIGT's constant a_h which I mentioned just now, we find:

$$r = 1650;$$

here we must bear in mind that this value applies to the particular sodiumflame to which my measurements relate; r must, as well as a_h , depend on the density of the sodiumvapour in the flame.

DRUDE tries in his book to fix limits, between which the value of r must lie. He finds a lower limit by deducing from theory the proportion between the quantity of light, which the absorbing sodiumflame itself begins to emit under the influence of incident radiation, and the quantity of incident light which is absorbed. This proportion he finds to be $0,126/r$. From the fact that reversal of a sodiumline is possible, he concludes that this proportion must be considerably smaller than 1, and he therefore fixes the lower limit for the value of r by assuming:

$$r > 10.$$

A higher limit is found by DRUDE from the consideration of the phenomena of interference. He deduces theoretically the value of the coefficient of damping γ of the free vibrations of the electron and finds for this:

$$\gamma = 0,6 \cdot r \cdot 10^{-7}.$$

Now this coefficient must be small, as with great phase-differences interference-phenomena can still be observed. With sodiumlight interference-phenomena have been observed with a phase-difference corresponding with 200000 wavelengths; therefore 200000γ must still be smaller than 1, therefore in this case:

$$r < 100.$$

It is evident that this result is not at all incompatible with the value of r which I calculated above. In order to observe interference-phenomena with such great phase-differences it has been necessary to use a source of light showing very narrow sodiumlines; with

the width of the sodiumlines to which my measurements relate (which was about 1 Angström-Unit) the greatest phase-difference with which interference-phenomena can be observed is one corresponding with 3000 wavelengths; the higher limit is therefore raised to 7000, so that r must in this case lie between 10 and 7000, which it really does according to the calculations given above.

Some further deductions which can be made from the comparison of VOIGT's equations with those given by DRUDE, have already been given on pp. 90—95 of my doctoral thesis, with reference to LORENTZ's paper in the Report of the *Congrès International de Physique*, held in Paris in 1900, and I will here only refer the reader to that part of my thesis.

Physiology. — “A new law concerning the relation between stimulus and effect.” V. By DR. J. K. Å. WERTHEIM SALOMONSON. (Communicated by Prof. C. WINKLER.)

From the law connecting excitation and effect,

$$E = A(1 - \epsilon^{-B(R-C)}) \dots \dots \dots (1)$$

we may obtain by differentiating

$$\frac{dE}{dR} = AB \epsilon^{-B(R-C)}$$

or also

$$dR = \frac{dE}{AB} \epsilon^{B(R-C)} \dots \dots \dots (2)$$

Introducing differences instead of differentials, with this limitation that the differences should be very small, and taking according to FECHNER, ΔE , the differential sensation-threshold as a constant quantity, we obtain

$$\Delta R = k_1 \epsilon^{B(R-C)} \dots \dots \dots (3)$$

or, by putting the constant $\epsilon^{-BC} k_1 = k$

$$\Delta R = k \epsilon^{BR} \dots \dots \dots (4)$$

the latter formula containing an expression for the absolute differential threshold-value. We might employ this formula for psychical impressions of peripheral stimuli, if the peripheral stimulus had caused excitation of only peripheral neurones with equal stimulation-constants B , and moreover if all these neurones had been uniformly stimulated. Under a similar limitation we might also admit the validity of the formula for the relative differential threshold-value deduced from (4) by dividing both terms by R ; we then obtain:

$$\frac{\Delta R}{R} = k \frac{\epsilon^{BR}}{R} \dots \dots \dots (5)$$

As a rule, however, this formula may not be applied in the case of psychical processes, because the above-stated conditions have not been fulfilled. It is impossible to suppose the case of a peripheral stimulus hitting only one single peripheral neuron, or of one single group of neurones being exposed uniformly and with equal force to that stimulus.

Let us see, what happens when a sense-organ in the living human organism is subjected to a stimulus. For instance we may consider the action of pressure on the skin.

Suppose the compressing object to be in contact with a limited surface of the skin at the moment the pressure commences. We

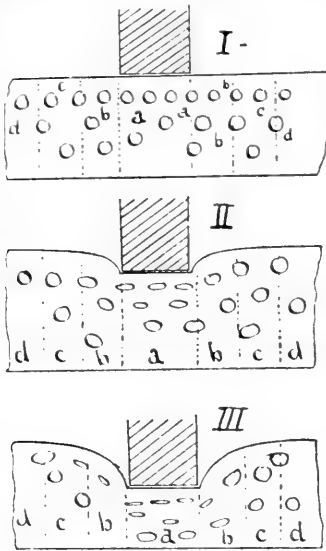


Fig. 1.

may take it for granted that all end-organs situated within the limited skin-surface in direct contact with the compressing object, undergo an equal and uniform pressure, and that in the case of this pressure being increased, its action will remain uniform. To the neurones connected with the nerve terminations *a, a, a, a*, our deduced law (5) may be therefore applied. As soon as the pressure increases the skin-surface will undergo a change of shape and be compressed (see fig. 1). This implies that nerve-endings *b, b*, situated outside of the originally compressed surface, will also enter into an excitatory state. If this deformation be a slight one, only the nearest end-organs *b, b* will be

compressed. By increased pressure the more distantly situated ones *c, c, d, d* etc. will also be stimulated. To all these end-organs, situated outside of the originally compressed surface, impulses are given, which are conducted to the central nervous system. From all the combined impressions finally results the sensation by which our judgment is decided.

The neurones connected with *b, b, c, c, d, d* etc. will likewise obey the law of stimulation and effect. The intensity of stimulus however is different for all these neurones, and also different from that for the neurones *a, a, a*. Therefore, whilst for the neurones *aaa*, the expression

$$q = \frac{dR}{R} = K \frac{\epsilon^{BR}}{R}$$

might be employed, we must use for the neura b, b, c, c, d, d etc. the expression

$$q_1 = K \frac{\epsilon^{Br_1}}{r_1}, \quad q_2 = K \frac{\epsilon^{Br_2}}{r_2}, \quad q_3 = K \frac{\epsilon^{Br_3}}{r_3} \text{ etc.}$$

As the stimuli r_1, r_2, r_3 etc. are proportional to R , we may substitute for these $m_1 R, m_2 R, m_3 R$ etc.

The question arises next: how shall we psychically combine these impressions in order to make use of them for the special purpose aimed at by our experiment, i. e. to decide whether two stimuli are different from one another? Summation or addition is out of the question: this would be in contradiction with the experience that by fixing our attention on a definite sensation, other sensations are weakened. It is clear that we will conform our judgment to that part of the sensation that is best fit for our purpose. Starting from this fact we may continue to treat the question mathematically.

In the first place it ought to be taken into consideration, that by increment of a stimulus not a small number of new peripheral neurones are stimulated, but generally a great many. In the case of a pressure e.g. not only nerve-endings lying sideways of the compressed surface, but also more profoundly situated end-organs will be acted upon by increased intensity of stimulus. For every individual neuron we shall have to put in another coefficient m . If

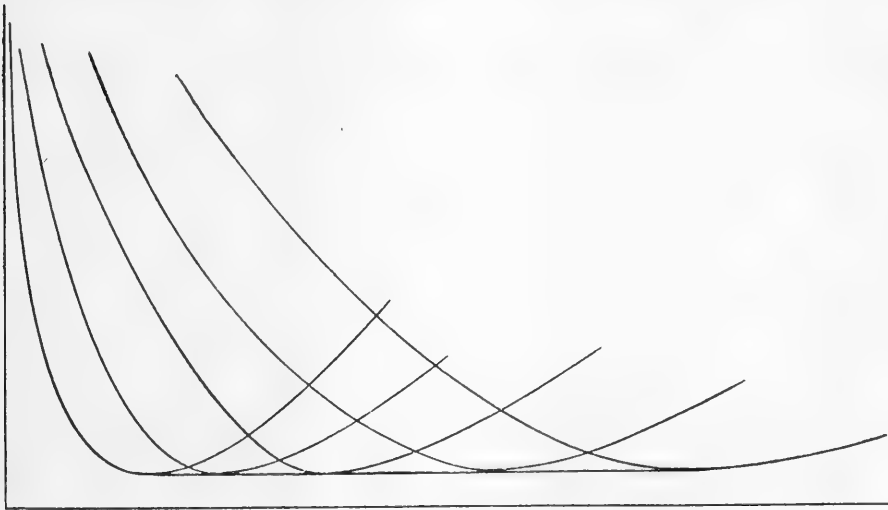


Fig. 2.

we construct therefore a great many curves q_1, q_2, q_3 all these curves will only be different on account of the constant m being changed. We now suppose the final judgment fixed each time by a part of a farther situated curve. Thence it may be concluded, that the

enveloping curve will represent the manner in which a judgment about the final result originates. To obtain the envelope of the group of curves $q = K \frac{\epsilon^{mBR}}{mR}$, if the constant m is changed, we put:

$$F = q - K \frac{\epsilon^{mBR}}{mR} \dots \dots \dots (6)$$

Calculating the value of m corresponding to $\frac{\partial F}{\partial m} = 0$, and substituting this value into the equation $F = 0$, we find the formula for the enveloping curve. We may state:

$$\frac{\partial F}{\partial m} = -\frac{K}{R} \cdot \epsilon^{mBR} \cdot \frac{mBR-1}{m^2} = 0 \dots \dots \dots (7)$$

From which follows $m = \frac{1}{BR}$, which substituted into $F = 0$, gives:

$$q = KB\epsilon \dots \dots \dots (8)$$

proving that the *relative differential thresholdvalue is constant*.

By this process we have deduced from our formula the law of WEBER.

From our deduction may be inferred that the area, wherein the law of WEBER prevails, is a limited one. The validity of this law commences within the area of the enveloping curve, and a look on the figure 2, will make it clear that the first part of the whole sensation-curve is given by the descending part of the curve

$q = K \frac{\epsilon^{BR}}{R}$. The horizontal part then represents the area within the limits of which the law of WEBER prevails, whilst in the case of very great intensities of stimuli the ascending part of the curve $q = K \frac{\epsilon^{BmR}}{mR}$ will appear.

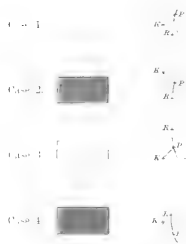
There remains still another conclusion to be drawn from our deduction. This latter was founded on the supposition that the increment-constant B was the same for all stimulated neurones. This, however, is highly improbable: in the most favourable cases we may only suppose that the B -coefficient of the homogenous neurones will possess approximatively the same value, from which follows that we may admit the law of WEBER at best as an approximation.

Finally it may be mentioned here that apart from the above-demonstrated correction for obtaining an approximation in the direction of the law of WEBER-FECHNER, probably still another means of correction exists in some of our sense-organs; I shall prove this in a later communication.

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SIDE OF THE LARGE VOLUMES.

Temperature slightly *higher* than the critical temperature of the solvent.



SIDE OF THE LARGE VOLUMES.

Temperature slightly *lower* than the critical temperature of the solvent.

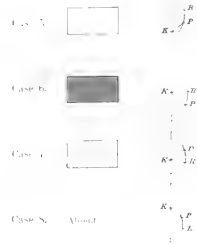


Fig. 1.

The figures relate to the P, v diagram.

K is the critical point of the solvent.

P the platpoint.

E the critical point of contact.

KP indicates the direction of the platpoint curve.

The lined curve represents the condal curve.

The dotted curve represents the spinodal curve.

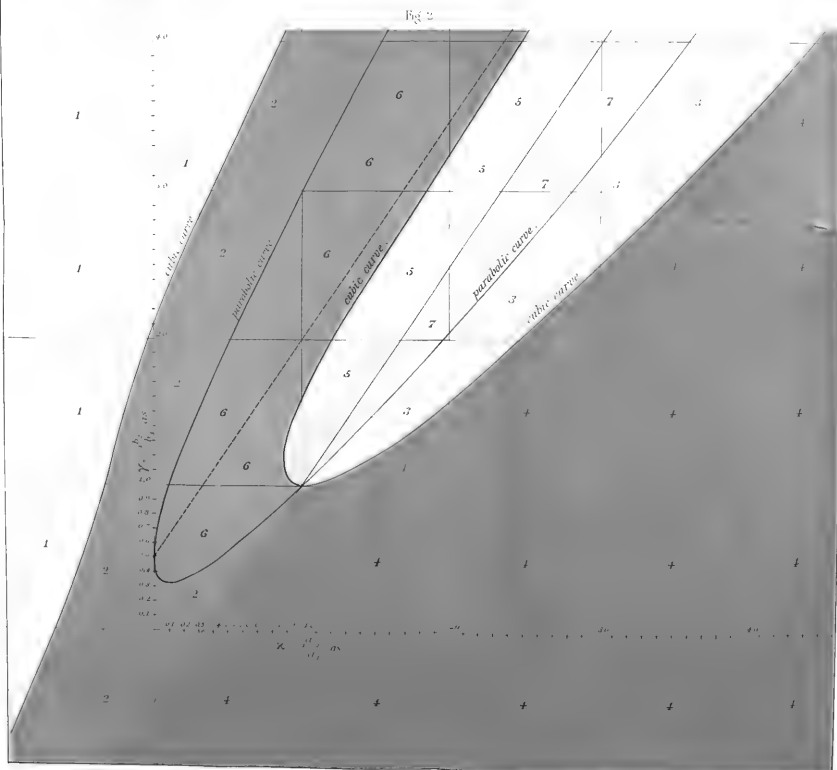


Fig. 2.

Physics. — “*Plaitpoints and corresponding plaitis in the neighbourhood of the sides of the ψ -surface of VAN DER WAALS.*” By Prof. D. J. KORTEWEG.

(Communicated in the Meeting of December 27, 1902).

FIRST DESCRIPTIVE PART.

1. As in my “*Théorie générale des plis*”¹⁾ I wish to precede in this paper the demonstrating part by a short summary of the obtained results.

As we know a plaitpoint may occur on the side $x=0$ of the ψ -surface of VAN DER WAALS,²⁾ which is represented by the equation :

$$\psi = -MRT \log(v - b_x) - \frac{a_x}{v} + MRT \{ x \log x + (1-x) \log(1-x) \} . \quad (1)$$

where :

$$a_x = a_1(1-x)^2 + 2 {}_1a_2 x(1-x) + a_2 x^2 = a_1 + 2({}_1a_2 - a_1)x + (a_1 + a_2 - 2 {}_1a_2)x^2, \dots \quad (2)$$

$$b_x = b_1(1-x)^2 + 2 {}_1b_2 x(1-x) + b_2 x^2 = b_1 + 2({}_1b_2 - b_1)x + (b_1 + b_2 - 2 {}_1b_2)x^2, \dots \quad (3)$$

This occurs only in the case that the temperature T corresponds with the critical T_k of the principal component; but in that case it occurs always. This plaitpoint coincides with the critical point of the principal component for which $v = 3 b_1$ and which in our figures we shall always represent by the symbol K ; the plaitpoint itself will be represented by P .

If the temperature varies, the plaitpoint and the corresponding plait can in general behave in two quite different ways. It will namely either, as is indicated by the *first* four cases on fig. I of the plate, on which the (v, x) projections of the sides of the ψ -surface are represented, at increase of temperature leave the v -axis and move to the inner side, therefore entering the surface, and disappear from the surface at decrease of temperature, or it will as in the *last* four cases of that figure, enter the surface at decrease and leave it at increase of temperature.

¹⁾ Archives Néerlandaises, T. 24 (1891) p. 295—368: La théorie générale des plis et la surface ψ de VAN DER WAALS dans le cas de symétrie. See there p. 320—368.

²⁾ We take here the equation of the ψ -surface as it has been originally derived by VAN DER WAALS, so without the empiric corrections which seem to be required to make the results agree quantitatively better with the experimental data. So is, for instance, a_x considered to be independent of the temperature, and all the results and formulae mentioned are founded on this supposition. It would not have been difficult to take such empiric corrections into account, as has really been done by VERSCHAFFELT and KESOM in their papers, to which we shall presently refer; but then the results were of course not so easily surveyed. Therefore I have preferred to leave them out of account, at least for the present.

And this different behaviour of the plaitpoint will necessarily be accompanied by a different behaviour of the connodal and spinodal curves. For they must always cut the v -axis at decrease of temperature, the connodal in the points of contact of the double tangent of the ψ, v -curve of the principal component, the spinodal in its two points of inflection; at increase of temperature above the critical temperature of the principal component, however, they get quite detached from the v -axis. In connection with this they turn in the first four cases of fig. 1 their convex sides, in the last four cases their concave sides towards the side $x = 0$ of the ψ -surface as is also indicated in the figure, where the connodal curves are traced, the spinodal curves dotted.

Fig. a.



At decrease of temperature a figure originates in the *first* four cases as is schematically given here in Fig. a. At *increase* of temperature, on the contrary, in the *last* four cases, the spinodal and connodal curves disappear from the surface at the same time with the plaitpoint itself.

Besides to this different behaviour it appeared however desirable, to pay attention to two other circumstances. *First* to the direction of the tangent in the plaitpoint, whether if prolonged towards the side of the large volumes, it inclines to the *inner* side of the ψ -surface, as in cases 1, 2, 5 and 6 of fig. 1, or whether it inclines to the *outer* side, as in the remaining four cases. For on this it will depend which of the two kinds of retrograde condensation will eventually appear¹⁾. But besides we have to pay attention to the question whether the plaitpoint, entering the ψ -surface, either at decrease or increase of temperature, will move towards the side of the larger volumes as in cases 1, 3, 5 and 7, or whether it will move towards that of the smaller volumes as in the other cases. In connection with this question we may point out here that the line KP in fig 1 of the plate may everywhere be considered as a small chord of the plaitpoint curve of the v, v -diagram and accordingly indicates the initial direction of that curve, which it has when starting from point K .

The three different alternatives, which we have distinguished in this way, give rise to the eight cases represented in fig. 1, and we may now raise the question on what it will depend which of these eight cases will occur at a given principal component with a given

¹⁾ See on these two kinds of retrograde condensation inter alia, the paper of VAN DER WAALS: "Statique des fluides (Mélanges)": in Tome I of the "Rapports présentés au congrès international de physique, réuni à Paris en 1900", page 606—609.

admixture; of course only in so far as with sufficient approximation the conditions are satisfied on which the derivation of the equation (1) of VAN DER WAALS rests.

2. The answer to this question is given in the graphical representation of fig. 2. It appears, namely, that the case which will occur, is exclusively determined by the quantities $\frac{1^a_2}{a_1} = \alpha$ and $\frac{1^b_2}{b_1} = \gamma$, which have already played a prominent part in my above mentioned "*Théorie générale des plis.*"

In accordance with this a α - and a γ -axis are assumed in fig. 2 of the plate and the regions where the points are situated whose α - and γ -values give rise to the appearance of each of these cases, are distinguished by different numbers and colours.

For instance the white region 1 indicates the α - and γ -values for which the plaitpoint enters the ψ -surface at rising temperature, moving from K to the side of the large volumes, while in the well-known way we can derive from its situation on the connodal curve on the right above the critical point of contact R (for which the tangent to the connodal curve runs parallel with the v -axis) that the retrograde condensation will be eventually of the second kind (i. e. with temporary formation of vapour) and also that the temporary vapour phase will have a larger amount of admixture than the permanent denser phase.

In the same way the blue field 5 indicates the α - and the γ -values for which the plaitpoint enters the ψ -surface at decrease of temperature, moving towards the side of the large volumes; whilst the retrograde condensation will be of the first kind and the temporary denser phase will show a smaller proportion of admixture than the permanent vapour phase.

3. When examining this graphical representation we see at once that one of the eight regions which were à priori to be expected, region 8, fails. From this follows that for normal substances the combination of retrograde condensation of the second kind and of a plaitpoint which enters the surface at decreasing temperature and moves towards the side of the small volumes, is not to be expected.

All the other seven regions, however, are represented in the graphical representation.

4. Further the point $\alpha = 1, \gamma = 1$, is remarkable, where no less than six regions meet. This point represents really a very particular

case, namely that in which the molecules of the admixture, both with regard to volume and to attraction, behave towards the molecules of the principal component exactly as if they were identical with these latter molecules.

If at the same time $a_2 = a_1$, $b_2 = b_1$, which is of course not involved in the above suppositions, it is easy to see that at decrease of temperature below the critical temperature the plait would suddenly appear all over the whole breadth of the ψ -surface.

Now it is true that every deviation from these equalities $a_2 = a_1$, $b_2 = b_1$ will prevent such a way of appearance, but it is evident that then the behaviour of plaitpoint and corresponding plait will depend on a_2 and b_2 , i.e. the first approximation for which the knowledge of α and γ is sufficient and which everywhere else suffices to make this behaviour known to us up to a certain distance from the side of the ψ -surface, fails here.

And also already in the *neighbourhood* of the combination of the values $\alpha = 1$, $\gamma = 1$, this first approximation will be restricted, to the immediate neighbourhood of the point K and of the critical temperature T_k of the principal component. When we are not in that immediate neighbourhood the influence of a_2 and b_2 , — of the former of these quantities specially, — will soon be felt. On the contrary for values of α or γ sufficiently differing from unity the considerations derived from the first approximation will probably be of force within pretty wide limits, at least in a qualitative sense.

5. Before proceeding to a discussion of the border curves between the different regions, we will shortly point out that we cannot attach an equally great importance to all the parts of the graphical representation. So all points lying left of the γ -axis relate to negative values of ${}_1a_2$, i.e. to the case that the molecules of principal component and admixture should repel each other, which is not likely to occur.

In the same way the negative values of γ , so of ${}_1b_2$, of the points below the α -axis, should be considered as having exclusively mathematical signification. If the relation, ${}_1b_2 = \frac{1}{2}(b_1 + b_2)$, should still be applied also for very unequal values of the b 's, then γ would even remain always larger than $\frac{1}{2}$ and so the part below the line $\gamma = \frac{1}{2}$ would lose its physical signification.

6. With regard to the border curves between the different parts, we have first to deal with the parabolic border curve separating the

regions containing blue (blue, green, purple) from the others. It touches the γ -axis in the point $z = 0, \gamma = \frac{1}{2}$. Its equation is:

$$(2\gamma - 3z + 1)^2 - 8(\gamma - z) = 0$$

or if we transfer the origin to the point $\gamma=1, z=1$ and therefore introduce the new variables: $z' = z-1; \gamma' = \gamma-1$, which brings about a simplification also for the other border curves, we get:

$$(2\gamma' - 3z')^2 - 8(\gamma' - z') = 0. \dots \dots \dots (4)$$

Then we have everywhere inside that parabola, so in the regions 5, 6, 7:

$$(2\gamma' - 3z')^2 - 8(\gamma' - z') < 0$$

and outside it in the regions 1, 2, 3, 4:

$$(2\gamma' - 3z')^2 - 8(\gamma' - z') > 0.$$

In consequence of this it depends on the situation inside or outside the parabola, whether on the corresponding ψ -surface the plaitpoint will enter the surface at *decrease* of temperature or at *increase* of temperature and whether the spinodal curves turn their convex or their concave sides to the side $x = 0$.

Fig. b.

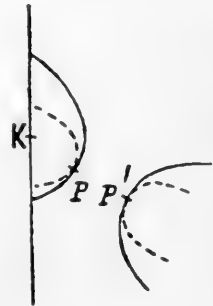


For points *on* the parabolic border curve the plaitpoint occurring in the point K at the critical temperature of the principal component, is to be considered as an homogeneous double plaitpoint at that moment. The projection on the v, x -surface appears then as is indicated in fig. b.

How the transition to this condition takes place may be made clear by the subjoined fig. c, which represents the same projection for a temperature slightly below that of the critical temperature of the principal component

for the case that the z - and γ -values indicate a point, which is still situated in the green region 6, but on the verge of the border curve of the yellow region 2.

Fig. c.



Very near the plaitpoint P we find here already a second plaitpoint P' , which at further decrease of temperature soon coincides with P .

If now the point in the green region approaches the border curve of the yellow region, the two points P coincide nearer and nearer to the critical temperature of the principal component and to the point K . On the border curve it takes place in the point K itself. *Beyond* the limit, in the yellow region, the plait of P does not develop any more and P' takes the place of P .

7. As second border we get in the graphical representation the straight line:

$$2 \gamma' - 3 \alpha' = 0. \quad (5)$$

It separates the regions containing red 3, 4 and 7, — for which $2 \gamma' - 3 \alpha' < 0$, and where the tangent in the plaitpoint, continued in the direction of the large volumes, inclines towards the side $x=0$ — from the others, where it inclines to the inner side of the ψ -surface.

As we saw before, this inclination determines the nature of the retrograde condensation. Not exclusively, however. For in the first four cases of figure 2 the result of the same way of inclination is in this regard exactly the opposite of that in the last four cases; hence the parabolic border curve acts here also as a separating curve; so that retrograde condensation of the first kind (i.e. with temporary formation of the denser phase) occurs in the regions 3, 4, 5 and 6, in the two first with greater proportion of the admixture in the temporary phase, in the two last the reverse, and on the contrary retrograde condensation of the second kind in the regions 1 and 2 (with a larger proportion in the temporary less dense phase) and 7 (with a smaller proportion in that same phase).

8. The third border curve is a cubic curve with the equation:

$$(2 \gamma' - 3 \alpha')^3 - 4 (4 \gamma' - 3 \alpha') (2 \gamma' - 3 \alpha') + 16 \gamma' = 0. \quad . . . (6)$$

It consists of two branches, which possess both on one side the common asymptote:

$$2 \gamma' - 3 \alpha' - 2 = 0 \quad (7)$$

and which run at the other side parabolically to infinity.

The right-side branch, whose shape resembles more or less a parabola, touches the curve $\gamma' = 0$ in the point $\alpha' = 0, \gamma' = 0 (\alpha=1, \gamma=1)$.

Between the two branches, so in the regions 2, 4 and 6:

$$(2 \gamma' - 3 \alpha')^3 - 4 (4 \gamma' - 3 \alpha') (2 \gamma' - 3 \alpha') + 16 \gamma' < 0;$$

in all the other regions of course > 0 .

In the former case the tangent KP to the plaitpoint-curve of the (v, x) -diagram is directed to the side of the small volumes, in the second to that of the large volumes.

If we, however, examine, whether e.g. at *decrease* of temperature the plaitpoint moves towards the large or towards the small volumes, the parabolic border curve acts again as separating curve.

It appears then that the plaitpoint moves towards the large volumes at decrease of temperature in the regions 2, 4, 5 and 7, at increase of temperature in the others.

9. The following table gives the characteristics for the different regions.

Region

1	$(2\gamma'-3\alpha')^2-8(\gamma'-\alpha')>0$	$2\gamma'-3\alpha'>0$	$(2\gamma'-3\alpha')^3-4(4\gamma'-3\alpha')(2\gamma'-3\alpha')+16\gamma'>0$
2	>0	>0	<0
3	>0	<0	>0
4	>0	<0	<0
5	<0	>0	>0
6	<0	<0	<0
7	<0	<0	>0

where :

$$\alpha' = \alpha - 1 = \frac{1a_2 - a_1}{a_1}; \quad \gamma' = \gamma - 1 = \frac{1b_2 - b_1}{b_1} \dots \dots (8)$$

A similar tabular survey of the physical properties of the regions seems superfluous, as these properties may be immediately read from the illustrations of fig. 1 of the unfolding plate.

10. It seems not devoid of interest to know how the breadths of the regions change with regard to each other, when continually increasing values of γ' are considered. An inquiry into this shows at once that the blue region 5, measured along a line parallel to the α -axis, has a limiting value for the breadth of $\frac{2}{3}$. All the other regions mentioned, however, continue to increase indefinitely, and do this proportional with $\sqrt{\gamma'}$ and in such a way that the yellow and the red region get gradually the same breadth and in the same way the green and the purple one, but that the breadth of the two first mentioned regions will amount to 0,732 of that of the two last mentioned.

If we also take the white region (reckoned e. g. from the γ -axis) into consideration then we find its breadth at first approximation to be proportional with γ' , so that it exceeds in the long run the other mentioned; the orange region keeps of course an infinite breadth.

The limiting values of the ratios may therefore be represented as follows :

$$\frac{\text{white}}{\infty} = \frac{\text{yellow}}{0,732} = \frac{\text{green}}{1} = \frac{\text{blue}}{0} = \frac{\text{purple}}{1} = \frac{\text{red}}{0,732} = \frac{\text{orange}}{\infty} \dots (9)$$

We may see that if we keep α constant and make γ to increase we always reach the white region, while reversively increase of α with constant γ leads finally to the orange region. Strong attraction between the molecules of the admixture and those of the principal

component promotes therefore in the long run the relations of case 4, large volume of the molecules of the admixture promotes those of case 1.

11. We may conclude this descriptive part with mentioning some formulae which we have obtained in the course of our investigation, and which will be derived in the second part. We do not, however, give them as new, as they must essentially agree with similar equations obtained by KEESOM¹⁾ and VERSCHAFFELT²⁾, if the simplifying hypotheses are introduced on which the original equation of the ψ -surface, used by us, rests. Nor does the way in which they are derived, in which the method of the systematic development into series is followed, differ considerably from that of VERSCHAFFELT.

In these formulae we have restricted the number of notations as much as possible. They only hold at approximation in the neighbourhood of point K and of the critical temperature T_k of the principal component.

We shall first give expressions for the radii of curvature $R'_{sp.}$ and $R'_{conn.}$ of the projections on the (v, x) -surface of the spinodal and connodal curves in the plaitpoint; from which appears that the radius of curvature of the connodal curve in the neighbourhood of the point K is at first approximation three times as great as that of the spinodal.

$$R'_{sp.} = \frac{3}{2} b_1^2 [(2\gamma' - 3\alpha')^2 - 8(\gamma' - \alpha')] \dots \dots \dots (10)$$

$$R'_{conn.} = \frac{9}{2} b_1^2 [(2\gamma' - 3\alpha')^2 - 8(\gamma' - \alpha')] = 3R'_{sp.} \dots \dots (11)$$

These radii of curvature are here considered as being positive when both curves turn their convex sides to the v -axis as in the cases 1—4 of fig. 1 and negative in the cases 5—7.

We may shortly point out here that the corresponding radii of curvature on the ψ -surface itself, on account of the strong inclination of the tangential plane in the neighbourhood of the v -axis, are quite different and much smaller, though the relation 1 : 3, of course

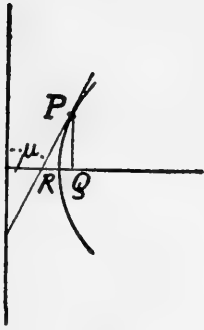
1) W. H. KEESOM. "Contributions to the knowledge of VAN DER WAALS'S ψ -surface. V. The dependence of the plaitpoint constants on the composition in binary mixtures with small proportions of one of the components". Proc. Royal Acad. IV. p. 293—307. Leiden, Comm. phys. Lab. N^o. 75.

2) J. E. VERSCHAFFELT. "Contributions to the knowledge of VAN DER WAALS'S ψ -surface. VII. The equation of state and the ψ -surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components". Proc. Royal Acad. V, p. 321—350, Leiden, Comm. Phys. Lab. N^o. 81.

continues to exist. They even become zero when the plaitpoint coincides with the critical point K , so that both curves have then a cusp.

12. The knowledge of the radius of curvature $R_{conn.}$ is of importance specially because it may be used in connection with the formula:

Fig. d.



$$tg \mu = \mu = \frac{1}{4b_1} (2\gamma' - 3\kappa') v_P, \dots \dots \dots (12)$$

through which we know the small angle which the tangent of the plaitpoint forms with the v -axis, to calculate in a very simple way the differences in density and volume between the phases of the plaitpoint P and the critical point of contact R at first approximation ¹⁾.

According to fig. *d* we have, within the indicated limit of accuracy:

$$v_P - v_R = PQ = PR = \mu R'_{conn.} = \frac{9b_1}{8} (2\gamma' - 3\kappa') [(2\gamma' - 3\kappa')^2 - 8(\gamma' - \kappa')] v_P \dots (13)$$

$$x_P - x_R = RQ = \frac{1}{2} \mu^2 R'_{conn.} = \frac{9}{64} (2\gamma' - 3\kappa')^2 [(2\gamma' - 3\kappa')^2 - 8(\gamma' - \kappa')] v_P^2 \dots (14)$$

13. We proceed now to give the formulae relating to the plait-points phase at a temperature T , which does not differ much from the critical temperature T'_k of the principal component.

They are:

$$v_P = \frac{4}{(2\gamma' - 3\kappa')^2 - 8(\gamma' - \kappa')} \cdot \frac{T - T'_k}{T_k} \dots \dots \dots (15)$$

$$v_P - 3b_1 = \frac{3}{8} b_1 \{ (2\gamma' - 3\kappa')^3 - 4(4\gamma' - 3\kappa')(2\gamma' - 3\kappa') + 16\gamma' \} v_P \dots (16)$$

$$\frac{p_P - p_k}{p_k} = \{ (2\gamma' - 3\kappa')^2 - 4\gamma' + 2\kappa' \} v_P \dots \dots \dots (17)$$

By means of (15) we may transform (13) and (14), so that they become:

$$v_P - v_R = \frac{9b_1}{2} (2\gamma' - 3\kappa') \frac{T - T'_k}{T_k} \dots \dots \dots (18)$$

and

$$x_P - x_R = \frac{9}{16} (2\gamma' - 3\kappa')^2 v_P \frac{T - T'_k}{T_k} \dots \dots \dots (19)$$

¹⁾ A similar method is given by KEESOM at the conclusion of the before-mentioned paper of VERSCHAFFELT.

to which we add:

$$\frac{p_P - p_R}{p_k} = -\frac{1}{4b_1} (2\gamma' - 3\alpha')^2 (v_P - v_R) x_P = -\frac{9}{8} (2\gamma' - 3\alpha')^3 \frac{T - T_k}{T_k} x_P \quad (20)$$

14. We shall conclude with giving some formulae relating to coexisting phases, where the index *one* refers to the liquid-, the index *two* to the gas phase. Where the index fails, we may arbitrarily take the value for the one or for the other coexisting phase; either because it is indifferent at the degree of approximation used, or because the formula will equally hold for either state.

$$v_1 = 3b_1 - 3b_1 \sqrt{-4 \frac{T - T_k}{T_k} + [(2\gamma' - 3\alpha')^2 - 8(\gamma' - \alpha')]x} \quad (21)$$

$$v_2 = 3b_1 + 3b_1 \sqrt{-4 \frac{T - T_k}{T_k} + [(2\gamma' - 3\alpha')^2 - 8(\gamma' - \alpha')]x} \quad (22)$$

$$\frac{p - p_k}{p_k} = 4 \frac{T - T_k}{T_k} + 2 (2\gamma' - 3\alpha') x \quad \dots \quad (23)$$

$$x_2 - x_1 = \frac{1}{4b_1} (2\gamma' - 3\alpha') (v_2 - v_1) x \quad \dots \quad (24)$$

$$\begin{aligned} \frac{1}{2} (v_2 + v_1) - 3b_1 &= -\frac{54}{5} b_1 \frac{T - T_k}{T_k} + 3b_1 \left\{ \frac{7}{5} [(2\gamma' - 3\alpha')^2 - 8(\gamma' - \alpha')] + \right. \\ &+ \left. \frac{1}{8} [(2\gamma' - 3\alpha')^3 - 24(\gamma' - \alpha')(2\gamma' - 3\alpha') + 16(3\gamma' - 2\alpha')] \right\} x \quad \dots \quad (25) \end{aligned}$$

in which formula (23) holds also for non-coexisting phases.

SECOND DEMONSTRATING PART.

Transformation of the ψ -surface and preliminary development into series.

15. We begin with a transformation of the ψ -surface by introducing the following variables:

$$v' = \frac{v - 3b_1}{3b_1}; \quad t' = \frac{T - T_k}{T_k}; \quad \psi' = \frac{\psi}{MRT_k}; \quad \dots \quad (26)$$

which means that we henceforth measure the volume v' from the critical volume and with that volume as unit, the temperature in the same way with regard to the critical temperature $T_k = \frac{8a_1}{27b_1MR}$ and the free energy ψ' with MRT_k as unit.

If we moreover put:

$$\frac{{}_1a_2 - a_1}{a_1} = \kappa'; \quad \frac{{}_1b_2 - b_1}{b_1} = \gamma'; \quad \frac{a_2 - a_1}{a_1} = \lambda'; \quad \frac{b_2 - b_1}{b_1} = \sigma'; \quad . \quad (27)$$

we find easily from (1), (2) and (3) for the equation of the new surface: ¹⁾:

$$\psi' = -(1+t') \log 3b_1 (b_x' + v') - \frac{a_x'}{1+v'} + (1+t') \{x \log x + (1-x) \log (1-x)\}, \quad (28)$$

where

$$a_x' = \frac{9}{8} + \frac{9}{4} \kappa' x - \frac{9}{8} (2 \kappa' - \lambda') x^2 (29)$$

$$b_x' = \frac{2}{3} - \frac{2}{3} \gamma' x + \frac{1}{3} (2 \gamma' - \sigma') x^2, (30)$$

further:

$$p = - \frac{\partial \psi}{\partial v} = - \frac{MRT_k}{3b_1} \cdot \frac{\partial \psi'}{\partial v'} = - \frac{8}{3} p_k \frac{\partial \psi'}{\partial v'} (31)$$

16. For investigations in the neighbourhood of the sides it is desirable to develop the expression for ψ' so far as possible according to the powers of x . We write therefore:

$$\psi' = (1+t') x \log x + \chi_0 + \chi_1 x + \chi_2 x^2 + \dots . . . (32)$$

where in finite form ²⁾

$$\chi_0 = - (1+t') \log b_1 (2+3v') - \frac{9}{8(1+v')} (33)$$

$$\chi_1 = (1+t') \left(\frac{2\gamma'}{2+3v'} - 1 \right) - \frac{9\kappa'}{4(1+v')} (34)$$

$$\chi_2 = (1+t') \left[\frac{2\gamma'^2}{(2+3v')^2} - \frac{2\gamma' - \sigma'}{2+3v'} + \frac{1}{2} \right] + \frac{9(2\kappa' - \lambda')}{8(1+v')} (35)$$

¹⁾ If we wanted to consider a_x as function of the temperature, the simplest way of doing this would be by writing the second term of the second member: $\frac{a'_x(1 + \epsilon_1 t' + \epsilon_2 t'^2 + \dots)}{1 + v'}$. The formula $T_k = \frac{8 a_1}{27 b_1 MR}$ would continue to

hold unmodified for the critical temperature of the principal component, provided we take for a_1 the value it has at that critical temperature. With CLAUSIUS' hypothesis that a_x is inversely proportionate to T , we should get $\epsilon_1 = -1$; $\epsilon_2 = +1$. Also (29) continues to hold and the modifications in the developments into series and in the formulae derived from them would be easy to apply.

²⁾ In this form they may be used for investigations concerning the conditions at the side of the ψ -surface at temperatures greatly differing from the critical temperature of the principal component, as are made by KEESOM: Contributions to the knowledge of the ψ -surface of VAN DER WAALS. VI. The increase of pressure at condensation of a substance with small admixtures. Proc. Royal Acad. IV, p. 659—668; Leiden, Comm. phys. Lab. No. 79.

or, after development into series with respect to the powers of v' :

$$\begin{aligned} \chi_0 = & -(1+t') \log 2b_1 - \frac{9}{8} - \left(\frac{3}{8} + \frac{3}{2}t' \right) v' + \frac{9}{8} t' v'^2 - \frac{9}{8} t' v'^3 + \\ & + \frac{9}{64} (1+9t') v'^4 - \frac{63}{160} v'^5 + \dots \end{aligned} \quad (36)$$

$$\begin{aligned} \chi_1 = & (1+t')(\gamma'-1) - \frac{9}{4} \alpha' - \frac{3}{4} \left[(2\gamma'-3\alpha') + 2\gamma't' \right] v' + \\ & + \frac{9}{4} \left[(\gamma'-\alpha') + \gamma't' \right] v'^2 - \frac{9}{8} (3\gamma'-2\alpha') v'^3 + \dots \end{aligned} \quad (37)$$

$$\chi_2 = \frac{1}{2}(1+t')[(1-\gamma')^2 + \sigma'] + \frac{9}{8}(2\alpha'-\lambda) - \frac{3}{8}(4\gamma'^2 - 4\gamma' + 2\sigma' + 6\alpha' - 3\lambda)v' + \dots \quad (38)$$

for which last expression we write:

$$\chi_2 = \sigma_0 + \sigma_1 t' + \sigma_2 v' + \dots \quad (39)$$

Determination of the plaitpoint and classification of the different possible cases.

17. For calculating the coordinates v'_P and x_P of the plaitpoint we have the following relations: ¹⁾

$$m \frac{\partial^2 \Psi'}{\partial x^2} + \frac{\partial^2 \Psi'}{\partial v' \partial x} = 0 \quad (40)$$

$$m \frac{\partial^2 \Psi'}{\partial v' \partial x'} + \frac{\partial^2 \Psi'}{\partial v'^2} = 0 \quad (41)$$

$$m^3 \frac{\partial^3 \Psi'}{\partial x^3} + 3m^2 \frac{\partial^3 \Psi'}{\partial v' \partial x^2} + 3m \frac{\partial^3 \Psi'}{\partial v'^2 \partial x} + \frac{\partial^3 \Psi'}{\partial v'^3} = 0 \quad (42)$$

where m represents ²⁾ the tangent of the angle formed by the (v', x) -projection of the common tangent of spinodal and connodal curve in the plaitpoint with the v' -axis.

If by means of (32), (36) and (37) we introduce in these equations everywhere the values of the differential quotients at first approximation, in which, as appears, m , x_P and v'_P may be treated as small quantities of the same order, we find:

$$\frac{m}{x_P} - \frac{3}{4} (2\gamma' - 3\alpha') = 0 \quad (43)$$

¹⁾ D. J. KORTEWEG. Ueber Faltenpunkte. Wiener Sitzungsberichte, Bd. 98, Abt. II, (1889), p. 1171.

²⁾ See l. c. p. 1163.

$$-\frac{3}{4}(2\gamma'-3\kappa')m + \frac{9}{4}t' + \frac{9}{2}(\gamma'-\kappa')x_P = 0 \quad . . . \quad (44)$$

$$-\frac{m^3}{x_P^2} + \frac{27}{2}(\gamma'-\kappa')m - \frac{27}{4}t' + \frac{27}{8}v'_P - \frac{27}{4}(3\gamma'-2\kappa')x_P = 0, \quad (45)$$

from which it is easy to deduce :

$$m = \frac{3}{4}(2\gamma'-3\kappa')x_P, \quad \quad (46)$$

$$x_P = \frac{4}{(2\gamma'-3\kappa')^2 - 8(\gamma'-\kappa')}t', \quad \quad (47)$$

$$v'_P = \frac{1}{8}[(2\gamma'-3\kappa')^3 - 4(4\gamma'-3\kappa')(2\gamma'-3\kappa') + 16\gamma']x_P, \quad . . \quad (48)$$

The formulae (12), (15) and (16) of the first descriptive part of this paper may be derived from these formulae by means of the reverse transformation into the original ψ -surface with the aid of the formulae (26). Applying equation (31) we may also derive formula (17). In the course of this we get first at formula (23), which is given at the end of the descriptive part as serving also for the calculation for coexisting phases. The last statement might be objected to, because for those phases not v' but v'^2 is a quantity of the same order as x and t' ; but this objection loses its force when we observe that in $\frac{\partial\psi'}{\partial v'}$ no term occurs with v'^2 alone.

18. From these formulae (46), (47) and (48) follows now immediately the classification of the plaitpoints according to the eight cases and all the particularities of the corresponding graphical representation, as described in § 2—9. It is only necessary to say a few words about the construction of the cubic border curve.

$$(2\gamma'-3\kappa')^3 - 4(4\gamma'-3\kappa')(2\gamma'-3\kappa') + 16\gamma' = 0. \quad . . . \quad (49)$$

A closer examination of this equation shows, namely, that the curve possesses a double point, i.e. the point at infinity of the straight line $2\gamma'-3\kappa'=0$. A simple parameter representation is therefore possible and it is really obtained by putting

$$2\gamma'-3\kappa' = s \quad \quad (50)$$

from which follows:

$$s^3 - 4s(s+2\gamma') + 16\gamma' = 0 \quad \quad (51)$$

hence:

$$\gamma' = \frac{s^2(s-4)}{8(s-2)} \quad ; \quad \kappa' = \frac{s^3 - 8s^2 + 8s}{12(s-2)} \quad \quad (52)$$

The points of the left-side branch are then given by the values of s between $+\infty$ and 2, those of the right-side branch by the others.

For $s = 2$ we get the two infinite branches belonging to the asymptote:

$$2\gamma' - 3\alpha' = 2 \dots \dots \dots (53)$$

19. Nor do we meet with any difficulties in the calculation of the breadth-relations of the regions for very large values of γ' mentioned in § 10.

For the cubic curve we may put:

$$3\alpha' = 2\gamma' + k\sqrt{\gamma'} \dots \dots \dots (54)$$

through which its equation passes into:

$$(-k^3 + 8k)\sqrt{\gamma'} + 16 - 4k^2 = 0 \dots \dots \dots (55)$$

from which appears that for very large values of γ' we find $-2\sqrt{2}$, 0 and $+2\sqrt{2}$ for k . We get therefore for the leftside branch of the cubic curve approximately:

$$\alpha' = \frac{2}{3}\gamma' - \frac{2}{3}\sqrt{2} \cdot \sqrt{\gamma'} \dots \dots \dots (56)$$

and for that on the right-side:

$$\alpha' = \frac{2}{3}\gamma' + \frac{2}{3}\sqrt{2} \cdot \sqrt{\gamma'} \dots \dots \dots (57)$$

while of course the middle branch with asymptote corresponds with $k = 0$. For this branch we have:

$$\alpha' = \frac{2}{3}\gamma' - \frac{2}{3} \dots \dots \dots (58)$$

In a similar way we find for the parabolic border curve:

$$\alpha' = \frac{2}{3}\gamma' \pm \frac{2}{9}\sqrt{6} \cdot \sqrt{\gamma'} \dots \dots \dots (59)$$

Taking this into consideration we may equate the breadth of the yellow region at infinity to $\frac{2}{9}(3-\sqrt{3})\sqrt{2} \cdot \sqrt{\gamma'}$, that of the green one to $\frac{2}{9}\sqrt{6} \cdot \sqrt{\gamma'}$, that of the blue one to $\frac{2}{3}$, that of the purple one again to $\frac{2}{9}\sqrt{6} \cdot \sqrt{\gamma'}$ and that of the red one to $\frac{2}{9}(3+\sqrt{3})\sqrt{2} \cdot \sqrt{\gamma'}$ from which the relations of equation (9) easily follow, while $\sqrt{3} - 1 = 0.732$.

The spinodal curve.

20. The equation of the spinodal curve is found by elimination of m from (40) and (41). We must, however, take into account, when writing these two equations, that v' along the spinodal curve must be considered to be of the order \sqrt{v} , so that the terms with v'^2 must also be taken into consideration.

We get then:

$$\frac{m}{x_{sp.}} - \frac{3}{4} (2\gamma' - 3\kappa') = 0 \dots \dots \dots (60)$$

and

$$-\frac{3}{4} (2\gamma' - 3\kappa') m + \frac{9}{4} t' + \frac{27}{16} v_{sp.}'^2 + \frac{9}{2} (\gamma' - \kappa') x_{sp.} = 0 \dots (61)$$

from which follows for the equation of the spinodal curve:

$$v_{sp.}'^2 - \frac{1}{3} [(2\gamma' - 3\kappa')^2 - 8 (\gamma' - \kappa')] x_{sp.} + \frac{4}{3} t' = 0 \dots (62)$$

This is, however, its equation on the ψ' -surface. In order to know it on the original ψ -surface, we must transform it with the aid of (26) into

$$(v_{sp.} - 3b_1)^2 - 3b_1^2 [(2\gamma' - 3\kappa')^2 - 8 (\gamma' - \kappa')] x_{sp.} + 12b_1^2 t' = 0 \dots (63)$$

For that of the circle:

$$(v - 3b_1)^2 + (x - R - \sigma)^2 = R^2, \quad (\sigma \text{ small})$$

we may write with the same approximation:

$$(v - 3b_1)^2 - 2Rx + 2R\sigma = 0,$$

from which we may immediately derive the expression (10) for the radius of curvature of the (v, x) projection of the spinodal curve.

The two first connodal relations. Equation of the connodal curve.

21. We shall now take $P_1(v_1, v'_1)$ and $P_2(v_2, v'_2)$, for which $v'_2 > v'_1$, as denoting two corresponding connodes.

We put then:

$$v'_1 = v'' - \eta; \quad v'_2 = v'' + \eta; \quad x_1 = x'' - \xi\eta; \quad x_2 = x'' + \xi\eta; \quad \dots (64)$$

hence:

$$v'' = \frac{1}{2} (v'_1 + v'_2); \quad \eta = \frac{1}{2} (v'_2 - v'_1); \quad x'' = \frac{1}{2} (x_1 + x_2); \quad \xi = \frac{x_2 - x_1}{v'_2 - v'_1}; \quad (65)$$

where therefore (x'', v'') indicates a point halfway between the two connodes and ξ denotes the tangent of the angle which the projection on the (v', x) -surface of the join of the connodes forms with the v' -axis.

It is then easy to anticipate, and it is confirmed by the calculations, that all these quantities v'' , x'' and ξ with the exception of η , are of the same order with each other and with t' ; on the contrary not η but η^2 is of this same order.

22. Taking this into consideration the *first* connodal relation :

$$\frac{\partial \psi'_2}{\partial x_2} = \frac{\partial \psi'_1}{\partial x_1} \dots \dots \dots (66)$$

yields at first approximation :

$$\log (x'' + \xi \eta) - \frac{3}{4} (2\gamma' - 3\alpha') (v'' + \eta) = \log (x'' - \xi \eta) - \frac{3}{4} (2\gamma' - 3\alpha') (v'' - \eta) \dots (67)$$

or also, subtracting on either side $\log x''$:

$$\log \left(1 + \frac{\xi \eta}{x''} \right) - \frac{3}{2} (2\gamma' - 3\alpha') \eta = \log \left(1 - \frac{\xi \eta}{x''} \right) \dots (68)$$

or, as $\frac{\xi \eta}{x''}$ is a small quantity of the order of η , we get after development into series and division by η :

$$\xi = \frac{3}{4} (2\gamma' - 3\alpha') x'' \dots \dots \dots (69)$$

in which we shortly point out that this formula passes into formula (46) in the plaitpoint, and further that it leads immediately to formula (24) of the descriptive part.

In the same way the *second*¹⁾ connodal relation :

$$\frac{\partial \psi'_2}{\partial v_2} = \frac{\partial \psi'_1}{\partial v_1} \dots \dots \dots (70)$$

yields at approximation :

$$\begin{aligned} & - \frac{3}{8} - \frac{3}{2} t' + \frac{9}{4} t' (v'' + \eta) + \frac{9}{16} (v'' + \eta)^3 - \frac{3}{4} (2\gamma' - 3\alpha') (x'' + \xi \eta) + \\ & + \frac{9}{2} (\gamma' - \alpha') (v'' + \eta) x'' = - \frac{3}{8} - \frac{3}{2} t' + \frac{9}{4} t' (v'' - \eta) + \frac{9}{16} (v'' - \eta)^3 - \\ & - \frac{3}{4} (2\gamma' - 3\alpha') (x'' - \xi \eta) + \frac{9}{2} (\gamma' - \alpha') (v'' - \eta) x'', \dots \dots \dots (71) \end{aligned}$$

or, after reduction and division by η :

¹⁾ We must here have recourse to the terms of the order $t'^{\frac{3}{2}}$ or η^3 , as all those of lower order cancel each other. For the sake of clearness we have kept $(v'' + \eta)$ and also $(v'' - \eta)$ together, though it is evident, that we may write e.g. for $(v'' + \eta)^3$ at once η^3 on account of the difference in order of v'' and η .

$$\frac{9}{2} t' + \frac{9}{8} \eta^2 - \frac{3}{2} (2\gamma' - 3\alpha') \xi + 9 (\gamma' - \alpha') x'' = 0, \quad (72)$$

from which follows in connection with (69):

$$\eta^2 - [(2\gamma' - 3\alpha')^2 - 8 (\gamma' - \alpha')] x'' + 4 t' = 0. \quad (73)$$

23. This formula yields at once the radius of curvature of the (v, x) -projection of the connodal curve. We need only observe that according to definition:

$$v'_{conn.} = v'' \pm \eta; \quad x_{conn.} = x'' \pm \xi \eta; \quad (74)$$

so at first approximation:

$$\eta = \pm v'_{conn.} = \pm \frac{v_{conn.} - 3b_1}{3b_1}; \quad x'' = x_{conn.} \quad (75)$$

Substitution of these last relations in (73) now yields immediately the equation of the connodal curve and in exactly the same way as for the spinodal curve we find from it the value of the radius of curvature R_{conn} given in formula (11). A further explanation of the way in which the knowledge of this value leads to the formulae (13) and (14) need not be given here, nor need we explain the derivation of the formulae (18) and (19), (21) and (22).

But the derivation of formula (20) will detain us for a moment; we require, namely, for it a more accurate expression for p than that given in formula (23). If we therefore develop (31) as far as needful for the purpose, we find ¹⁾:

$$p = -\frac{8}{3} p_k \left(-\frac{3}{8} - \frac{3}{2} t' + \frac{9}{4} t' v' - \frac{3}{4} (2\gamma' - 3\alpha') x + \frac{9}{2} (\gamma' - \alpha') v' x \right), \quad (76)$$

or:

$$\frac{p - p_k}{p_k} = 4 t' - 6 t' v' + 2 (2\gamma' - 3\alpha') x - 12 (\gamma' - \alpha') v' x, \quad (77)$$

thence:

$$\frac{p_P - p_R}{p_k} = -6 t' (v'_P - v'_R) + 2 (2\gamma' - 3\alpha') (x_P - x_R) - 12 (\gamma' - \alpha') (v'_P - v'_R) x_P, \quad (78)$$

for, with regard to the last term, the difference of x_P and x_R is slight compared to that between v'_P and v'_R .

¹⁾ It might appear as if $\frac{9}{16} v'^3$ ought also to be inserted in the following expression, but it is easy to see that this term leads to a small quantity of higher order than those that will occur in the final result.

It is now easy to find:

$$x_P - x_R = \frac{1}{2} m (v'_P - v'_R) = \frac{3}{8} (2\gamma' - 3\alpha') x_P (v'_P - v'_R), \quad (79)$$

either by paying attention to the fact that we have in Fig. *d*, § 12 (see the first descriptive part), if applied to the (v', x) -diagram, with a sufficient degree of approximation:

$$RQ = PQ \cdot \text{tg } RPQ = PQ \cdot \text{tg } \frac{1}{2} \mu = \frac{1}{2} \cdot PQ \cdot \text{tg } \mu = \frac{1}{2} \cdot PQ \cdot m,$$

or by application of the formulae (13) and (14), observing that $v_P - v_R = 3b_1 (v'_P - v'_R)$.

This yields by substitution in (78):

$$\frac{P_P - P_R}{P_k} = \left(-6t' + \frac{3}{4} (2\gamma' - 3\alpha')^2 x_P - 12(\gamma' - \alpha') x_P \right) (v'_P - v'_R), \quad (80)$$

or finally substituting for t' its value from (47):

$$\frac{P_P - P_R}{P_k} = -\frac{3}{4} (2\gamma' - 3\alpha')^2 x_P (v'_P - v'_R) = -\frac{1}{4b_1} (2\gamma' - 3\alpha')^2 x_P (v_P - v_R), \quad (81)$$

from which we immediately derive formula (20), applying (18).

The third connodal relation.

24. We have now obtained the principal formulae. For the sake of completeness, however, we shall treat here also the third connodal relation, the more so as this leads to a new determination of the formulae (47) and (48), which puts the former to the test.

This third relation reads:

$$\psi'_2 - x_2 \frac{\partial \psi'_2}{\partial x_2} - v'_2 \frac{\partial \psi'_2}{\partial v'_2} = \psi'_1 - x_1 \frac{\partial \psi'_1}{\partial x_1} - v'_1 \frac{\partial \psi'_1}{\partial v'_1}. \quad (82)$$

We first transform $\psi' - x \frac{\partial \psi'}{\partial x} - v' \frac{\partial \psi'}{\partial v'}$, with the aid of (32). It proves to be necessary to keep all terms up to the order t^3 or η^5 . So we find:

$$\psi' - \frac{\partial \psi'}{\partial x} - v' \frac{\partial \psi'}{\partial v'} = -(1+t')x + \chi_0 - v' \frac{\partial \chi_0}{\partial v'} - v' x \frac{\partial \chi_1}{\partial v'} - \left(\chi_2 + v' \frac{\partial \chi_2}{\partial v'} \right) x^2. \quad (83)$$

From this follows:

$$\begin{aligned} \psi'_2 - x_2 \frac{\partial \psi'_2}{\partial x_2} - v'_2 \frac{\partial \psi'_2}{\partial v'_2} = & -(1+t')(x'' + \xi\eta) - (1+t') \log 2b_1 - \frac{9}{8} - \frac{9}{8} t' (\eta^2 + 2v''\eta) + \\ & + \frac{9}{4} t' \eta^3 - \frac{27}{64} (\eta^4 + 4v''\eta^3) + \frac{63}{40} \eta^5 + \frac{3}{4} [(2\gamma' - 3\alpha') + 2\gamma't'] (\eta + v'') (x'' + \xi\eta) - \\ & - \frac{9}{2} (\gamma' - \alpha') (\eta^2 + 2v''\eta) (x'' + \xi\eta) + \frac{27}{8} (3\gamma' - 2\alpha') \eta^3 x'' - \sigma_0 (v''^2 + 2x''\xi\eta) - 2\sigma_2 \eta v''^2. \end{aligned} \quad (84)$$

If we equate this to the corresponding expression for

$$\psi'_1 - x_1 \frac{\partial \psi'_1}{\partial x_1} = v'_1 \frac{\partial \psi_1}{\partial v'_1},$$

which is obtained by changing η into $-\eta$, we get, dividing by η :

$$\begin{aligned} & -2\xi - 2t\xi - \frac{9}{2}t'v'' + \frac{9}{2}t'\eta^2 - \frac{27}{8}v''\eta^2 + \frac{63}{20}\eta^4 + \frac{3}{2}(2\gamma' - 3\alpha')x'' + 3\gamma'tx'' + \\ & + \frac{3}{2}(2\gamma' - 3\alpha')v''\xi - 9(\gamma' - \alpha')\xi\eta^2 - 18(\gamma' - \alpha')v''x'' + \\ & + \frac{27}{4}(3\gamma' - 2\alpha')\eta^2x'' - 4\sigma_0x''\xi - 4\sigma_2x''^2 = 0. \quad \dots \quad (85) \end{aligned}$$

At first approximation this yields:

$$\xi = \frac{3}{4}(2\gamma' - 3\alpha')x''.$$

This relation is, however, identical with the relation (69) which is derived from the first connodal relation. So we cannot draw any further conclusion from equation (85) without bringing it into connection with the first connodal relation; but for this it is required to introduce a further approximation for the latter.

Second approximation of the first connodal relation.

25. From the first connodal relation in connection with the equation

$$\frac{\partial \psi'}{\partial x} = 1 + t' + (1 + t') \log x + \chi_1 + 2\chi_2x + \dots \quad (86)$$

the following relation may easily be derived, if we take into account the terms up to the order t^2 or η^3 :

$$\begin{aligned} & (1 + t') \log \frac{1 + \frac{\xi\eta}{x''}}{1 - \frac{\xi\eta}{x''}} - \frac{3}{2}(2\gamma' - 3\alpha')\eta - 3\gamma'\eta t' + 9(\gamma' - \alpha')v''\eta - \frac{9}{4}(3\gamma' - 2\alpha')\eta^3 + \\ & + 4\sigma_0\xi\eta + 4\sigma_2\eta x'' = 0 \quad \dots \quad (87) \end{aligned}$$

Within the same order of approximation we have however:

$$\log \frac{1 + \frac{\xi\eta}{x''}}{1 - \frac{\xi\eta}{x''}} = \frac{2\xi\eta}{x''} + \frac{2\xi^3\eta^3}{3x''^3}.$$

In the second term of the second member of this equation, however, we may safely make use of the first approximation furnished by equation (69). Taking this into account (87) passes after multiplication with x'' and division by η into:

$$2\bar{\xi} + 2\bar{\xi}' + \frac{9}{32}(2\gamma' - 3\alpha')^3 \eta^2 v'' - \frac{3}{2}(2\gamma' - 3\alpha')v'' - 3\gamma'v''t' + 9(\gamma' - \alpha')v''x'' - \frac{9}{4}(3\gamma' - 2\alpha')\eta^2 v'' + 4\sigma_0 \bar{\xi}v'' + 4\sigma_2 v''^2 = 0. \quad (88)$$

Further reduction of the third connodal relation.

Derivation of equation (25) of the first descriptive part.

26. By addition of (85) and (88) we find: ¹⁾

$$-\frac{9}{2}t'v'' + \frac{9}{2}t'\eta^2 - \frac{27}{8}v''\eta^2 + \frac{63}{20}\eta^4 - 9(\gamma' - \alpha')\bar{\xi}\eta^2 - 9(\gamma' - \alpha')v''x'' + \frac{3}{2}(2\gamma' - 3\alpha')v''\bar{\xi} + \frac{9}{32}[(2\gamma' - 3\alpha')^3 + 16(3\gamma' - 2\alpha')]\eta^2 v'' = 0. \quad (89)$$

When we add to this relation (72), which is deduced from the second connodal relation, after having multiplied it with v'' , we can divide by η^2 and we get:

$$\frac{9}{2}t' - \frac{9}{4}v'' + \frac{63}{20}\eta^2 - 9(\gamma' - \alpha')\bar{\xi} + \frac{9}{32}[(2\gamma' - 3\alpha')^3 + 16(3\gamma' - 2\alpha')]v'' = 0. \quad (90)$$

Making use of (69) we may solve the quantity v'' from this equation :

$$v'' = 2t' + \frac{7}{5}\eta^2 + \frac{1}{8}[(2\gamma' - 3\alpha')^3 - 24(2\gamma' - 3\alpha')(\gamma' - \alpha') + 16(3\gamma' - 2\alpha')]v'', \quad (91)$$

or finally with the aid of (73):

$$v'' = -\frac{18}{5}t' + \left\{ \frac{7}{5}[(2\gamma' - 3\alpha')^2 - 8(\gamma' - \alpha')] + \frac{1}{8}[(2\gamma' - 3\alpha')^3 - 24(2\gamma' - 3\alpha')(\gamma' - \alpha') + 16(3\gamma' - 2\alpha')] \right\} v''. \quad (92)$$

from which equation (25) follows immediately with the aid of (65) and (26).

In this way we have found the starting-point of the curve in the (v, x) -diagram described by the point halfway between the points which represent coexisting phases. The tangent in that starting point also is now known.

¹⁾ Remarkable is the disappearance of the terms derived from $\alpha_2 x^2$, which makes also λ' and ϑ' , i. e. $\frac{\alpha_2}{\alpha_1}$ and $\frac{b_2}{b_1}$ disappear from the result. We have tested the truth of this in different ways.

*A new determination of the plaitpoint, independent
of the preceding one.*

27. It is now easy to obtain such a determination with the aid of (73) and (91). For in the plaitpoint we have:

$$\eta = 0 \quad ; \quad x'' = x_p \quad ; \quad v'' = v'_p.$$

From (73) follows immediately (47); from (91):

$$v'_p = 2t' + \frac{1}{8} [(2\gamma' - 3\alpha')^3 - 24(2\gamma' - 3\alpha')(\gamma' - \alpha') + 16(3\gamma' - 2\alpha')]_{x_p}; \quad . \quad (93)$$

from which in connection with (47) we find again (48).

Physics. — “*Some remarkable phenomena, concerning the electric circuit in electrolytes*”. By Mr. A. H. SIRKS. (Communicated by Prof. H. A. LORENTZ).

On etching of metal-alloys by means of the electric current, as communicated in the proceedings of the meeting of September 27, 1902, I met with a great difficulty. In some cases the hydrogen developed at the kathode was very troublesome, namely when, instead of escaping immediately it divided itself in small bubbles through the liquid and stuck to the object to be etched used as anode. This obstacle was overcome by surrounding the kathode with fine brass-gauze, so that the gasbubbles were compelled to escape directly in this case. The gauze was hung up apart, consequently there was no contact, whatever, with one of the electrodes. The etching being finished, copper proved to have been precipitated on the wires of the gauze, which deposit was almost conform to the shape of the electrodes.

This was still more visible at a second etching-experiment with the same copper-alloy: a small cup was placed under the anode, which partly hung in it. Again on the gauze a copper-deposit was perceptible, which showed at the lower side a distinctly designed horizontal margin, nearly as high as the brim of the cup.

It was to be expected, that copper should precipitate on the gauze, placed between the electrodes, as the whole apparatus can be considered as two voltameters, connected in series¹⁾. But, why is by this electrolysis not the whole side of the gauze, facing the anode, coppered, as is the case with the kathode by any ordinary electrolysis?

To answer this question the experiments were altered somewhat.

¹⁾ The anode and the side of the gauze facing it, are the electrodes of one, the other side of it and the kathode, those of the other voltameter.

Instead of water acidulated with sulphuric-acid a saturated solution of copper-sulphate was used as electrolyte: the electrodes were formed in future by two equally large Dutch bronze coins. The back part of these coins and the battery-wires, to which they were soldered, were varnished, as far as they were immersed in the electrolyte, in order to be sure, that, during the electrolysis, the facing-sides only served as pole-plates. The gauze tube was left away and a screen of platinum (4×4 c.m.), hung up isolated, placed just amidst the electrodes, who were 4 c. m. from each other. If a copper-deposit might appear on the platinum, this could be ascribed to electrolytic actions only. Very soon after the circuit was closed (intensity $\pm 0,3$ amp; voltage of the battery = 4 volts) there came on the piece of platinum facing the anode a sharply bounded copper-deposit, which, by continuation of the experiment, changed of thickness exclusively and not of size. The experiment was continued for 2 days; still the results remained the same.

Now I resolved to remove the platinum screen between the electrodes, to do the experiment over again and repeat this several times. The deposits obtained in all these cases were not exactly of the same size. The smallest deposit (diam. 18 mM) was obtained by hanging the screen between the electrodes (diam. 19 mM.), from which we can conclude to a small gradual contraction to the middle.

If two electrodes of different shape were used, then, by removing the platinum screen from the anode to the kathode, the copper-deposit passed from the shape of one electrode into that of the other. This was very clearly visible by using a nut as anode and a square piece of sheet-copper as kathode. The hexagonal copperdeposit gradually took a square shape.

Superficially one would be inclined to suppose, that the only thing, that has happened is the locally making of sections of the envelope of the two electrodes by means of the screen, but considering, that, if electricity passes from one electrode to the other, the stream-lines divide through the whole fluid — the current-density is only larger within the above-mentioned envelope — it will be obvious, that there must have been another cause, which made some stream-lines prefer to take the way round the screen to the shorter one through it. Considering, that the resistance of the platinum can be neglected in regard to that of the longer way through the fluid, the explanation of the deviation of these stream-lines can only be found in the polarisation, caused by the screen of platinum.

To prove the supposal, that stream-lines are going out from the electrodes in all directions, the following experiment may serve: The

anode was hung in a platinum cup, which must replace the platinum diaphragm and was therefore partly filled with the electrolyte. Directly the circuit was closed, the inside of the cup was evenly coppered, as high as the surface of the liquid, while at the outside an intense gas-development took place, which was soon impossible to be observed well, as on account of the polarisation the current-intensity was considerably decreasing. In some cases from 0,9 amp. to 0,02 amp. If on the reverse the kathode was hung in the cup, the development of gas took place at the whole inside. Half of the outside of the cup facing the anode was partly and unevenly covered with a copper-deposit.

When making the experiment with a sheet of platinum (5×5 cm.), dividing the glass in two equal parts, the results were just the same. Here also the platinum was entirely covered with precipitated copper. At a distance of the electrodes of about 10 m.m., the copper-deposit was pretty evenly spread over the platinum. At a smaller distance of the electrodes (4 m.m.) there came between the electrodes on the platinum a distinct circular deposit, while the copper precipitated on the remainder of the screen was very faint. A same deposit perfectly corresponds with the sections of the stream-lines we should expect.

The same results were obtained, when using two diaphragms dividing the cup into three parts. At the first experiment two diaphragms were used, completely shutting off the fluid and connected with a copper-wire. The side of the first diaphragm, facing the anode, counting from the anode to the kathode, was entirely coppered; the side of the other one, facing the kathode, was covered with gas-bubbles.

At a second experiment only the connecting wire was taken away. The sides of both diaphragms, facing the positive electrode, were entirely covered with a copper-deposit. On the other sides gas was developing.

At a third experiment two platinum screens (4×4 cm.) were used, thus not shutting off the fluid completely, but connected, however, with a copper-wire. The same circular copper-deposit came on the first screen, facing the anode, but, when breaking the connection the same side of the second screen was, on the contrary, entirely covered with copper.

The latter phenomenon can be explained in this manner: The copper-ions, leaving the anode, yielded their charge to the first screen, over which it is entirely distributed and which, over the whole side, facing the kathode, serves in its turn as anode towards the second screen, which is coppered over the whole surface. If the second

screen was larger than the first, then, the side of the former, facing the anode, was coppered for a part about as large as the latter.

Then, the experiment was repeated with a screen, dividing the basin into two equal parts, but having a small hole in the middle. Just as a part of the stream-lines in some of the former experiments went round the screen, so here a very great contraction of the stream-lines towards the hole may be expected. Some of them will deviate from their straight way preferring the way through the hole, to the way through the screen. This is confirmed by a circular part of the screen remaining uncovered.

The following data are the results of a series of experiments, taken with holes of different size.

Diameter of the hole.	Diameter of the uncovered part.
1 mm.	7 mm.
2 "	10 "
4 "	14 "
5 "	17 "
8 "	25 "
15 "	whole screen uncovered.

distance between electrodes 3 cm., diameter of electrodes 19 mm.

If the smaller screen is taken, so that stream-lines can also go round it as well, then the uncovered part is considerably smaller. The diameter of it was 3 mm. at a 1 mm. diameter of the hole.

It is worth notice, that, while the electro-motive force remained the same, the current-intensity increased on increasing the diameter of the aperture. If for instance at the experiment with the smallest hole (diam. 1 mm.) the intensity after the beginning of the polarisation was 0,1 amp., it amounts under the same circumstances to 0,3 amp., when using the screen with the biggest hole.

It is curious, that at the first experiment a copper-deposit was seen on the case of brass gauze surrounding the kathode, though properly it is nothing but a screen with a great number of small holes. According to what is said before, it might have been expected, that all the stream-lines would pass from the anode through the holes of the case to the kathode and therefore not form any deposit on the gauze. In connection with this, some more experiments were taken with different sorts of brass gauze, but already by using the next size — stitches of 2 mm² and 0,3 mm. wires — no traces of copper were precipitated.

If the way through the fluid was made considerably longer, then, in some cases, the current still seemed to prefer this round-

about way to the undoubtedly shorter one through the screen. This was done in the following way: Again the anode was hung in a platinum cup, over the brim of which hung a bent glass-tube, filled with the copper-sulphate solution, thus forming the connection between the electrolyte at the inner- and outer side of the cup. Even if a capillary tube was used, a deviation was observed in the copper-deposit, namely: a part of the cup near the lower end of the tube was not coppered, this, however, only when the tube was hung over that place on the brim of the cup between the electrodes. A 3 mm. tube, however, caused a deviation of the deposit, even, if the tube was hung over the brim of the cup on the prolongation of the centre-line of the electrodes.

Of course, there must be some relation between the coppering of the inner surface of the cup in these cases and the circular deposit on the screen. It must be possible, therefore, to pass gradually from one deposit into the other. Instead of the cup a cylinder of platinum, having a diameter of 4 cm., was used, which at the bottom was melted in a basin with paraffine and projected from the fluid. The anode was hung in it again. The circuit being closed, the inside of the cylinder was of course coppered again as far as it was immersed in the electrolyte (50 mm.). Then a vertical cleft of 1 mm. wide and 1 mm. high was made in the cylinder on the extension-line of the centres of electrodes. A part of the inner wall round the cleft remained again uncovered. When gradually giving the cleft a height of 20 mm., the uncovered part took the form of an ellipse, till at a height of 25 mm. a strip of 8 mm. wideness was not covered with copper, along the whole height, i. e. 50 mm., of the electrolyte. When still enlarging the cleft, the deposit gradually receded more from the margins and after unfolding the cylinder into a plane it finally took the already known circular form again.

To make the explanation, given of the deviation of the stream-lines on account of the polarisation of the platinum, more acceptable, the experiments were made with different electromotive forces by inserting resistance. By means of a resistance box, connected parallel with the voltameter, the terminal voltage of the latter could be increased. The current-intensity could be read on a milli-ampere-meter, joined in circuit with the voltameter. As long as the potential difference was less than the electro-motive force of the polarisation, nothing was precipitated. After more resistance had been inserted in the resistance box, a current began to pass through the voltameter, but without forming a deposit on the sheet of platinum, although the experiment was carried on some hours. For that reason this current

could not have chosen its way through the screen and must have gone therefore round it. If some more resistance was inserted, then a deposit came gradually on the screen, smaller and more uneven than in the ordinary case, but also taking the normal size and thickness as formerly, when going on inserting more resistance.

Different salts were used as electrolyte, in none however, a deposit was so easily formed as in cupric sulphate. The phenomenon, when using this salt, was so clear, that once a deviation in the shape of the deposit was observed, because the wire which was connected to the anode, was not sufficiently insulated. In saturated solutions of zinc-, aluminium-, nickel-, cobalt-, ferrous- and ferric sulphate deposits were formed, one clearer than the other even if in all these cases the constant current-intensity was secured by inserting resistance.

Chlorides were also used as electrolytes. In chlorides of zinc and cadmium exactly the same circular deposit was formed, but in those metals, which can form more than one chloride (e.g. iron), a secondary phenomenon always appeared. When a solution of cupric-chloride was electrolysed, copper precipitated on the kathode; when, however, a platinum screen was put between the electrodes, again a circular deposit of a white substance was formed on the screen, quickly getting green in the air and being hygroscopic then; probably it might have been cuprous chloride, afterwards becoming cupric chloride again. When using a solution of Hg Cl_2 as electrolyte a white deposit of Hg Cl_2 came on the platinum. A solution of Au Cl_3 gave conformable results; a brown red deposit was formed. Using H_2PtCl_6 and a screen of gold-leaf, a yellow brown one was formed on the latter. When a solution of ferric chloride was used no deposit was ever formed. The explanation may be found perhaps in the solubility of ferrous chloride which is precipitated on the platinum as copper before.

Though in many of the former cases an explanation could be found in the polarisation, yet, however, there is one thing, that cannot be explained, i. e. the curious sharp margins of the deposit. It seems as if the stream-lines keep their original direction within a certain tubular surface also in the presence of the platinum screen, while this screen has a strong influence on the lines outside of it, which change their direction and go round the screen. Perhaps the explanation may be found by calculating the course of the circuit, but I am not able to do it.

In the making of all these experiments I have become indebted

to professor ARONSTEIN and professor SCHROEDER VAN DER KOLK for their assistance of various kinds and to these I tender my best thanks. Also to Professor H. A. LORENTZ, professor at the Leyden University, for his help and information.

Mineralogical Laboratory.
Polyt. School.

Delft, Jan. 1903.

(February 25, 1903).



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday February 28, 1903.

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C O N T E N T S.

J. P. KUENEN: "Critical phenomena of partially miscible liquids—ethane and methylalcohol"
(Communicated by Prof. H. KAMERLINGH ONNES), p. 473.

A. P. N. FRANCHIMONT: "On the so-called compounds of salts of sulphoncarboxylic acids with
sulphuric esters", p. 482.

JAN DE VRIES: "On the spheres of MONGE belonging to ordinary and tangential pencils or
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J. D. VAN DER WAALS JR.: "The variability with the density of the quantity b of the equation
of state". (Communicated by Prof. J. D. VAN DER WAALS), p. 487.

J. W. MOLL presents the dissertation of Dr. J. C. SCHOUTE: "Die Stelär-Theorie", p. 497.

H. KAMERLINGH ONNES: "Methods and apparatus used in the cryogenic laboratory. III. Bath
of very uniform and constant low temperatures in the cryostat", p. 502, (with 6 plates).

The following papers were read:

Physics. — "*Critical phenomena of partially miscible liquids — ethane
and methylalcohol.*" By J. P. KUENEN. (Communicated by
Prof. H. KAMERLINGH ONNES).

(Communicated in the Meeting of September 27, 1902).

Some years ago Mr. W. G. ROBSON and I began a systematic
investigation of the phenomena of condensation for mixtures of liquids
which do not mix in all proportions ¹⁾. Shortly afterwards Prof. VAN
DER WAALS communicated to this Society an important paper in which
he discussed our results ²⁾ and again in the second volume of his
treatise on the Continuity ³⁾ he devotes some pages to the conside-

¹⁾ Zeitschrift für Physik, Chemie 28, p. 342—365, Phil. Mag. (5) 48, p. 180—203.

²⁾ Kon. Ak. van Wet. Amsterdam 25th March 1899.

³⁾ Die Continuität etc. II. 1900, p. 184—192.

ration of the same phenomena. After the publication of Prof. VAN DER WAALS'S paper I approached him privately with some objections to his views to which he replied in the most courteous manner. Though not completely satisfied it seemed unnecessary at the time to publish my views until I should be in a position to add to our knowledge of the phenomena by further experiments.

I have recently resumed the investigation and the results obtained, though naturally far from complete, seem of sufficient importance to deserve an immediate publication and to be discussed in connection with previous experiments.

For various reasons we had fixed our choice on mixtures of hydrocarbons — first of all ethane — and alcohols. Briefly our results were as follows:

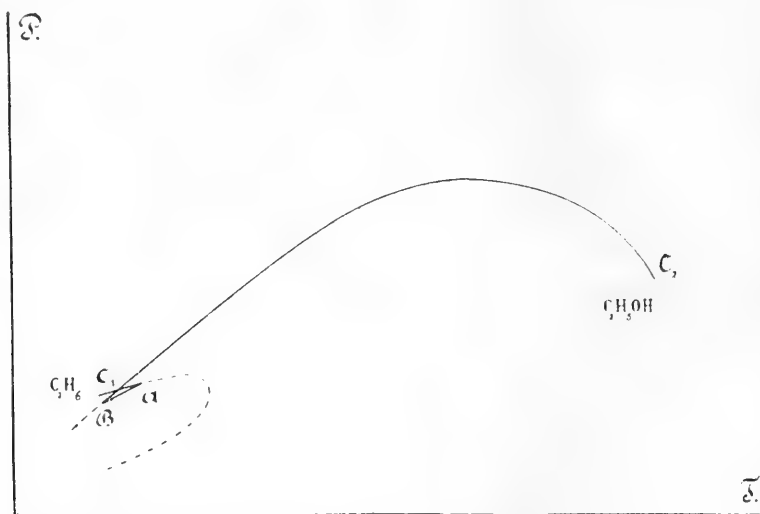


Fig 1.

For mixtures of ethane with ethyl-, propyl-, isopropyl- and butyl-alcohol there are two temperatures A and B (Fig. 1) between which three phases — two liquids and vapour — are possible and the critical (i.e. plaitpoint) curve accordingly consists of two branches, C_1A and C_2B , C_1 and C_2 representing the critical points of ethane and alcohol respectively and AB the three-phase curve. For ethyl-alcohol A and B are comparatively far apart; for the higher terms of the series these points gradually approach each other and with amyl-alcohol no separation into two liquids could be observed; in this case the critical curve was a continuous curve joining the two critical points C_1 and C_2 in the usual manner.

For mixtures of methylalcohol and ethane we found a branch C_1A

and a three-phase curve ending at A , as with the higher alcohols, but not a limit B below which the liquids mix in all proportions. The character of the other branch of the critical curve which begins at C_2 , the critical point of methylalcohol, therefore remained uncertain.

Prof. VAN DER WAALS's remarks concerned firstly the explanation of the behaviour of the first group of mixtures and secondly of the different behaviour of methylalcohol and the prediction of the phenomena outside the limits of our researches. The experiments communicated in this paper have reference to the latter problem.

First of all Prof. VAN DER WAALS shows how the two branches C_1A and C_2B may be made into one continuous curve by producing them in the region of the metastable and unstable conditions, a region which I shall call the "theoretical" region. In our paper we had pointed out that the phenomena were completely explained by the formation of a new subsidiary plait with plaitpoint emerging out of the main plait on the ψ -surface and the subsequent withdrawal and disappearance of the main plaitpoint¹⁾. Having regard to VAN DER WAALS's original investigation and to KORTEWEG's treatise²⁾ on the properties of the ψ -surface, the simplest interpretation appears to be to assume that at some temperature higher than T'_A a closed plait begins to develop on the spinodal curve, increasing in extent as the temperature falls, until one of its plaitpoints — that of the first kind³⁾ — at A pierces the connodal curve of the main plait, thus giving rise to the formation of the subsidiary plait and the three-phase triangle. On further fall of temperature the inner plaitpoint exchanges partners, so as to form a closed plait with that branch of the main plait on which the original plaitpoint lies: at B the connodal curve of the main plait begins to enclose this closed plait. We may moreover assume the latter to contract on further cooling and ultimately shrink to nothing⁴⁾. Transferring the above changes to the p - t -diagram we obtain the figure deduced from ours by Prof. VAN DER WAALS.

1) l. c. p. 358—359.

2) Arch. Néerl. 24 p. 295—368 in particular p. 316 etc.

3) Comp. KORTEWEG p. 67.

4) Whether this actually takes place seems at least doubtful. The *formation* of the plait on cooling is hardly open to doubt, seeing that at high temperatures the ψ -surface cannot show any abnormalities in the region under consideration: but this condition does not hold at low temperatures and the contraction of a closed plait on cooling is in contradiction with the rule enunciated by Prof. VAN DER WAALS regarding the influence of temperature on the extension of plaits.

The possibility of producing the theoretical curves in the p - t -diagram had escaped our notice ¹⁾.

In the first place Prof. VAN DER WAALS observes that the completed figure is in contradiction with the law previously deduced by him ²⁾ that a mixture of non associating substances may have a maximum or minimum critical temperature, but not both. To this point one of my objections refers. The law depends entirely on the simple characteristic equation, but apart from that it only refers to the critical point of the homogeneous mixtures and it must be looked upon as a possibility that the curve of the critical points — the plaitpoints — should have both a maximum and a minimum. Prof. VAN DER WAALS replies to this ³⁾ that near a maximum or minimum the two curves in question are so close to each other that no such difference between them can be admitted. This argument does not satisfy me. The two curves touch each other at points where a maximum or minimum *vapourpressure* exists and the two phases have the same composition, but points of that kind do not exist in the case under consideration. It is true that a maximum or minimum occurs on the plait when the connodal curve intersects the spinodal curve, but the character of these points is entirely different from that of the points referred to. The three-phase pressure for mixtures of ethane and the alcohol is between the vapourpressures of the components and there is thus no occasion for assuming the existence of another maximum or minimum. That being the case, there is no reason for a close resemblance between the two curves nor any

¹⁾ Note added to translation.

The above was written by me in the conviction which I then held that Prof. VAN DER WAALS'S views of the formation of the new plait — although arrived at in a different way — still agreed essentially with my own: indeed I do not even now see, how else the phenomena could be interpreted. From the paper contributed by him in the October-meeting of this society (critical phenomena of partially miscible liquids. Kon. Ak. van Wet. Amst. 25th Oct. 1902) it appears that such was not the case and that I ought to have been more careful in accepting the theoretical curve drawn by him as corresponding to the changes on the ψ -surface as understood by myself. Doubt never arose in my mind on this point at all and I never considered the question. Still I ought to have noticed that the theoretical curve has no vertical tangent at its extreme points, but ends in cusps, corresponding to the circumstance that the curvature of the connodal curve is the same in both plaitpoints of the closed plait. This is the only respect in which I think my paper requires emendation although some of my arguments would have been presented in a different manner had I realised how completely his views differed from mine.

²⁾ Arch. Néerl. 24 p. 23.

³⁾ Continuität II p. 188 l. 17.

ground why the "homogeneous" critical curve should have a loop as well as the plaitpointcurve.

I am strengthened in this opinion by the fact, that even in the "symmetrical" case Prof. KORTEWEG has come across similar peculiarities in the plait and it follows, that theoretically even those mixtures which obey VAN DER WAALS'S equation may have a critical curve with a loop in it.

I do not mean to maintain that the homogeneous curve in our case does not possess a loop or to deny the probability of Prof. VAN DER WAALS'S hypothesis according to which the association of the alcohols plays a part in producing the abnormality. What I want to point out is that it has not been proved that with normal mixtures the abnormality cannot occur, although it is very probable that this abnormality and in general the formation of two liquid layers -- while theoretically possible for normal mixtures with special values of the constants -- in reality occurs with associating substances only¹⁾.

The critical curve in the p, t -diagram having been completed in the way described one feels inclined to say with Prof. VAN DER WAALS that the case is one of a modified cross-plait and not of a true liquid-plait. According to VAN DER LEE'S experiments²⁾ the liquid-plait for mixtures of phenol and water has its plaitpoints turned in the direction of the positive volume-axis and above a certain temperature is entirely independent of the cross-plait. Prof. VAN DER WAALS seems inclined to look upon those properties as characteristic of the liquid-plait and to withhold this name from that part of the plait which in our case is turned towards the x -axis. It will appear presently that this view cannot very well be sustained so that at any rate this ground for drawing the distinction in question disappears. Still the peculiarity remains³⁾ that the critical curve is a continuous curve, at least when no account is taken of the objection urged above against joining the curves beyond B . Even then however it will be observed that on the ψ -surface two independent plaits exist completely or partly inside each other and thus when the ψ -surface itself is considered the contrast between our case and one in which a true liquid plait would exist disappears. Moreover the abnormality is ascribed to the same cause -- association -- as the formation of the liquid plait; if both are due to the same cause, one feels even less inclined to maintain a distinction in the nomenclature.

1) Continuität II p. 176. I doubt the possibility of deducing a relation between a_{12} on the one side and a_{11} and a_{22} on the other.

2) Zeitschr. Physik. Chemie, 33, p. 622, 630.

3) Continuität II p. 188.

The following may be added in further explanation: there is a well defined contrast between the two plaits as regards the causes of their existence. The cross-plait depends for its existence on the shape of the η -curves for the separate homogeneous mixtures, the liquid-plait on the other hand is due to the manner in which these curves change with the composition. In the formation of the latter plait association seems to be the principal factor. But notwithstanding this distinct contrast there must be a number of cases in which it will be impossible to say which kind of plait one is dealing with and to which sort of plait a given plaitpoint belongs. We shall presently come across a striking instance of this kind where a cross-plait with its plaitpoint gradually changes into a plait with its plaitpoint turned towards the x -axis from which it is impossible to withhold the name liquid-plate.

Let us now consider the case of methylalcohol and ethane. Before communicating the new results I will discuss Prof. VAN DER WAALS'S views of these mixtures. He assumes that the critical curve is again a continuous one but with a loop turned upwards this time instead of downwards as with the higher terms.¹⁾ There are some serious objections to this theory.

The critical curve, starting at the critical point of ethane C_1 , disappears from the practical part of the surface at A , as in the former case, and the part beyond can therefore only represent a theoretical plaitpoint which remains hidden, because at higher temperatures no three phases coexist. Beyond A the curve should therefore be dotted throughout, and it cannot be interpreted as in part real. In this case as in the other the shape of the curve was deduced by keeping in view the homogeneous critical point and a striking instance is afforded of how this curve does not give us any clue as to the shape of the real critical curve.

In the second place I think the bending upwards of the critical curve assumed in this case is open to doubt. At somewhat high temperatures there is probably no abnormality on the surface and no plait except the cross-plait: as the temperature falls a closed curve develops one of whose plaitpoints pierces the main plait at A and moves from there towards C_1 . As in the other mixtures the three-phase pressure is lower than the vapour pressure of ethane: it follows that the subsidiary plaitpoint is turned towards the x -axis and represents a maximum pressure on the closed plait. This being so the simplest supposition to make is that the other plaitpoint of

¹⁾ Comp. his diagram Kon. Ak. v. Wetensch. Amst. March 25th. 1899 p. 5.

this closed plait is one of minimum pressure: starting from this point the pressure on this plait passes through a maximum and a minimum successively and reaches its highest value in the real plait-point. In other words the theoretical part of the bent critical curve in the p,t -diagram should lie below the practical part, as with the other alcohols. This supposition seems so much simpler than the opposite one that I feel prompted to state the following rule: *when the three-phase pressure is between the vapour pressures of the components the theoretical critical curve bends downwards, when it is higher than the vapour pressures of the components (as with ether and water¹⁾) the curve bends upwards.*

In his book on the "Continuity"²⁾ the author discusses the probable behaviour of the mixtures at higher temperatures. Apart from a possible plaitpoint on the side of the small volumes on the liquid-plait, there is no practical plaitpoint left above A . Prof. VAN DER WAALS assumes that this condition will continue up to the critical point of methylalcohol, that the plait will close itself here, gradually contract and ultimately disappear either at the limiting liquid-volume or by its plaitpoint meeting with a possible liquid plaitpoint.

This expectation has not been realised by my experiments and must in itself be looked upon as improbable. The formation of the liquid-plait is ascribed to the association of methylalcohol. Above a certain temperature this abnormality has disappeared and in any case at the critical point it is for most substances very small. Considering the great difference between the critical temperatures of the two constituents of the mixture an admixture of ethane to methylalcohol cannot but lower the critical point, even if the mutual attraction of the components were comparatively great. As a matter of fact methylalcohol seems to have some association left at the critical point³⁾. But this association has the effect of making the mutual attraction appear even smaller and thus increases the probability of a lowering of the critical temperature by the addition of ethane. It follows that the cross-plait has to appear on the ψ -surface in the usual manner with fall of temperature, with its plaitpoint turned towards the ethane side.

In view of the fact that at low temperatures there is a liquid-

1) KUENEN and ROBSON l. c. p. 351.

2) Continuität II, p. 189 verv.

3) RAMSAY & SHIELDS, Zeitschr. Physik. Chemie 15, p. 115. Nobody seems to have observed as far as I know that the comparatively high value of the critical temperature of methylalcohol may be explained by association, as also the deviation from KOPF's law for the boiling points of series of organic substances.

plait there are still two possibilities with regard to the development of this cross-plait: (1) the plaitpoint continues by itself and gradually begins to form the closing plaitpoint of the liquid-plait which may disappear at the limiting liquid volume or (2) it disappears by meeting with a second plaitpoint belonging to an independent liquid-plait so that the two plaits then form one large one, with or without a closing plaitpoint on the liquid side.

The experiments confirm the above view of the effect of an admixture of ethane on the critical point of methylalcohol and as far as they go seem to show the first alternative to be the correct one. It appears that the general behaviour of mixtures of methylalcohol and ethane thus disclosed agrees with that of ether and water as predicted — without however any grounds being given — by KORTWEG ²⁾ and laid down in some *v-v*-diagrams. On the grounds set forth above I support this expectation as regards ether and water. *Addition of ether to water will lower the critical temperature.*

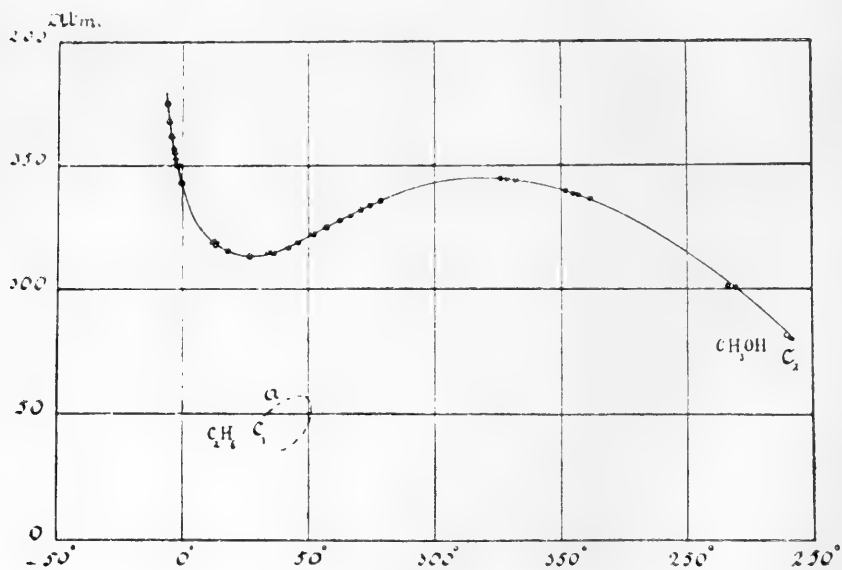


Fig. 2.

The results for methylalcohol and ethane are laid down in figure 2. I can give only a short explanation here. Starting from C_2 — the critical point of methylalcohol — the critical curve runs in a perfectly normal way at first, owing to the influence of the association being as yet insufficient. It ascends, passes through a maximum at 120° , and then falls, evidently tending towards the critical point

²⁾ Arch. Néerl. 24 p. 338—340.

of ethane; the association however becomes gradually stronger; the dip in the surface caused by this¹⁾ gradually modifies the shape of the cross-plait: the plaitpoint passes through a minimum pressure between 25° and 30° , and the critical curve then begins to rise rapidly. The end of the cross-plait thus changes without a discontinuity into a liquid-plait; in the mean time the main plait goes on developing on the approach of the critical point of ethane: as explained a small subsidiary plait is formed which appears at A on the practical part of the surface. Probably an exchange of plaitpoints occurs on the theoretical part, of the same nature as with the higher alcohols, the result being that at low temperatures the cross-plait is cut through by one self-contained liquid-plait. But as far as the phenomena are concerned this is entirely immaterial.

As far as the experiments could be carried (i. e. up to 275 atmospheres) the critical curve continued to rise towards the left, so that there is no indication of the existence of a different plaitpoint. The rapidity with which the mixing-pressure increases is truly remarkable.

If we compare the figures for methylalcohol and for the higher terms, a certain resemblance will be noticed, especially if we do not assume the contraction of the closed plait to nothing in the latter case. The association tends to produce the same modification in the usual diagram in both cases, but the acting causes appear to be much more effective with methylalcohol -- the stronger association of the alcohol, possibly a smaller mutual attraction or the influence suggested by Prof. VAN DER WAALS of the small molecular volume of the alcohol may contribute to this result. For this substance the plaitpoint remains outside the cross-plait at low temperatures, with the others it succeeds in disappearing inside. Whether inside this plait any changes take place similar to those occurring with methylalcohol on the practical part of the surface we cannot tell. But in any case I have assured myself that with ethylalcohol a new plaitpoint curve does not appear down to -78° : ethylalcohol and ethane remain miscible in all proportions.

Methylalcohol and ethane mix by pressure. In this respect they contrast with mixtures phenol and water for which the liquid plait above a certain temperature far below the critical region separates completely from the cross-plait and thus has a plaitpoint on the side of the positive v -axis. In view of the probable disappearance of the association at high temperatures it is possible that in the latter case

¹⁾ Continuität etc. II. p. 191.

further experiments will disclose a second plaitpoint on the liquid side of the plait, as predicted many years ago by VAN DER WAALS from the value of the volume-constants. I expect to be able to throw more light on this subject by the continuation of my investigation with the higher hydrocarbons. Ether and water behave in all probability in a manner similar to methylalcohol and ethane.

Chemistry. — “*On the so-called compounds of salts of sulphon-carboxylic acids with sulphuric esters.*” By Prof. A. P. N. FRANCHIMONT.

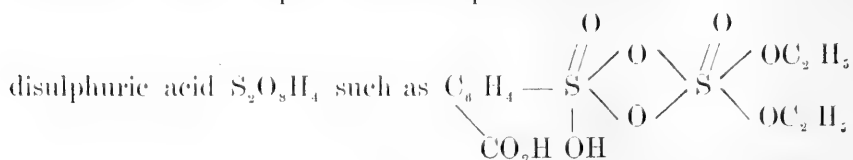
(Communicated in the meeting of January 31, 1903).

The first of this kind of compounds was obtained accidentally by LAUBE in 1879 in the laboratory of GEUTHER in Jena. He wanted to reduce sodium sulphonacetate with sodium amalgam and water, but after acidifying with sulphuric acid, evaporating, and extracting with absolute alcohol, he obtained an acid liquid which gave with barium carbonate a salt of the empirical composition $C_6 H_{11} Ba S_2 O_{10}$. This salt has, therefore, the composition of one molecule of barium sulphonacetate plus one molecule of ethyl sulphate plus one molecule of water and may, according to GEUTHER, be considered as a derivative of a disulphuric acid in which two hydrogen atoms have been replaced by ethyl groups and one OH group by the group CH_2-COOH . He obtained the same compound by digesting a mixture of sodium sulphonacetate, sodium-hydrogen sulphate and alcohol. The acid was called “*Diaethylsigdischweifelsäure*”. Acetic acid itself did not yield a similar compound.

In 1883, in the same laboratory, STENGEL successfully attempted to obtain a similar compound with metasulphobenzoic acid; the analysis gave the composition $C_{11} H_{14} O_7 S_2 Ba + 3\frac{1}{2} H_2O$. The acid was called “*Diaethylbenzödischweifelsäure*”. Analogous compounds were also obtained with methyl and propyl alcohol. Benzoic acid, however, did not give a similar compound and it is, therefore, attributed to the sulphonic acid group.

ENGELCKE obtained similar compounds with isethionic acid but not with benzenesulphonic acid and NITLACK did not obtain it with methylsulphonic acid.

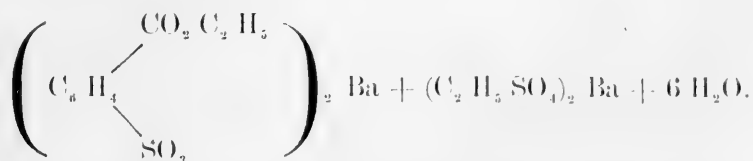
GEUTHER looked upon these compounds as salts of a derivative of



In BEILSTEIN'S "Handbuch", however, these compounds are described as double compounds of salts of sulphoncarboxylic acid with neutral sulphuric esters.

For a long time, however, I have felt serious objections to this theory. I had already repeated the experiments with sulphonacetic acid and metasulphobenzoic acid but did not obtain pure compounds. I was also unsuccessful in attempting a synthesis by means of the salts of sulphoncarboxylic acids and dimethyl- and diaethylsulphate. The phenomena observed during this research induced me to request Dr. ATTEMA to try to obtain compounds of the same empirical composition in a different manner, namely by bringing together in molecular proportions the barium salts of the acid esters of metasulphobenzoic acid with the barium salts of the alkylsulphuric acids. If in this proportion they yield a compound this ought then to have the same empirical composition as the last named compound.

Dr. ATTEMA now observed that on evaporating a solution containing in molecular proportions the barium salt of the ethyl ester of metasulphobenzoic acid and barium ethylsulphate, the greater portion of the ethylbarium salt of metasulphobenzoic acid was deposited first in beautiful crystals; after this a double compound of the two barium salts made its appearance in the form of large rosettes of tender needle-shaped crystals whilst from the motherliquor barium ethylsulphate was obtained. If an excess of barium ethylsulphate is taken for instance, 5 grams of the same to 1 gram of the salt of barium ester the double compound separates immediately and from the motherliquor barium ethylsulphate is obtained. The double compound cannot be recrystallised from water; its aqueous solution presents the same phenomena as one containing in molecular proportion the two salts; on evaporation, the salt of barium ester crystallises first, then the double compound and finally the barium ethylsulphate. As the double compound cannot be recrystallised from alcohol it was freed from motherliquor by strong pressure and analysed. The results of the analyses of three different preparations were concordant and agreed with the formula:



Dr. ATTEMA has afterwards repeated STENGEL'S method of preparing the compounds, but here he also obtained first the ethylbarium salt of metasulphobenzoic acid and afterwards, although less readily,

the double compound. An analogous result was obtained with the methyl compound.

We may, therefore, come to the conclusion that there exist no compounds of salts of sulphoncarboxylic acids with neutral sulphuric esters; there exist, however, double compounds of salts of the acid esters of sulphoncarboxylic acids with salts of the acid sulphuric esters. This result gives rise to a number of questions some of which Dr. ATTEMA intends answering by practical experiments. Both salts are alkyl-metallic salts of dibasic acids whose acidic functions (at all events in the case of metasulphobenzoic acid) have a very different power, whilst sulphuric acid as oxysulphonic acid is somewhat comparable to isethionic acid which also exhibits the property.

Mathematics. — “*On the spheres of MONGE belonging to ordinary and tangential pencils of quadratic surfaces.*” By Prof. JAN DE VRIES.

1. In Part I of the “Proceedings of the Section of Sciences” pages 305—310, I have developed, making use of FIEDLER’s cyclographic representation, some properties with respect to the system of the orthoptical circles of the conics of a linear system. By extending FIEDLER’s considerations to a four-dimensional space the corresponding case of the three-dimensional space might be treated. In the following essay the indicated extension on quadratic surfaces is arrived at analytically.

Given P the point of intersection of three mutually perpendicular tangent planes of the quadratic surface S^2 represented by the equation

$$a_{11}x^2 + a_{22}y^2 + a_{33}z^2 + 2a_{12}xy + 2a_{13}xz + 2a_{23}yz + 2a_{14}x + 2a_{24}y + 2a_{34}z + a_{44} = 0.$$

These three tangent planes form with every fourth tangent plane a tetrahedron circumscribed about S^2 that may be regarded as polar tetrahedron with respect to the point-sphere (isotropic cone) I^2 represented by

$$(x-x_1)^2 + (y-y_1)^2 + (z-z_1)^2 = 0.$$

So the invariant Θ belonging to S^2 and I^2 is equal to zero¹⁾. Therefore we have:

¹⁾ See a. o. SALMON-FIEDLER, Anal. Geom. des Raumes, 3d edition, vol. I, p. 253, where S^2 is represented by an ellipsoid.

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} & -x_1 \\ a_{12} & a_{22} & a_{23} & -y_1 \\ a_{13} & a_{23} & a_{33} & -z_1 \\ a_{14} & a_{24} & a_{34} & (x_1^2 + y_1^2 + z_1^2) \end{vmatrix} + \begin{vmatrix} a_{11} & a_{12} & 0 & a_{14} \\ a_{12} & a_{22} & 0 & a_{24} \\ a_{13} & a_{23} & 1 & a_{34} \\ a_{14} & a_{24} & -z_1 & a_{44} \end{vmatrix} +$$

$$+ \begin{vmatrix} a_{11} & 0 & a_{13} & a_{14} \\ a_{12} & 1 & a_{23} & a_{24} \\ a_{13} & 0 & a_{33} & a_{34} \\ a_{14} & -y_1 & a_{34} & a_{44} \end{vmatrix} + \begin{vmatrix} 1 & a_{12} & a_{13} & a_{14} \\ 0 & a_{22} & a_{23} & a_{24} \\ 0 & a_{23} & a_{33} & a_{34} \\ -a_1 & a_{24} & a_{34} & a_{44} \end{vmatrix} = 0.$$

If we represent the minor of a_{ik} in $\mathcal{L} = \sum \pm a_{11} a_{22} a_{33} a_{44}$ by A_{ik} , it ensues from this relation that the locus of the point P is indicated by the following equation (where the indices of the coordinates are left out)

$$A_{44} (x^2 + y^2 + z^2) - 2 (A_{14}x + A_{24}y + A_{34}z) + (A_{11} + A_{22} + A_{33}) = 0.$$

So the locus of the points of intersection of triplets of mutually perpendicular tangent planes of S^2 is a sphere (MONGE).

The tangential cone to S^2 with vertex P possessing three mutually perpendicular tangent planes, the tangent planes form according to a well-known property an infinite number of triplets of mutually perpendicular planes.

For $A_{44} = 0$ we find S^2 to be a paraboloid and the sphere of MONGE degenerates into a plane.

The obtained equation can be replaced by

$$\left(x - \frac{A_{14}}{A_{44}}\right)^2 + \left(y - \frac{A_{24}}{A_{44}}\right)^2 + \left(z - \frac{A_{34}}{A_{44}}\right)^2 = \frac{1}{A_{44}^2} \sum (A_{14}^2 - A_{11}A_{44}).$$

Now however $A_{11}A_{44} - A_{14}^2$ is equal to $(a_{22}a_{33} - a_{23}^2) \mathcal{L}^{-1}$

The radius of the sphere is indicated by the square root out of

$$-\frac{\mathcal{L}}{A_{44}^2} \sum (a_{22}a_{33} - a_{23}^2).$$

Consequently the sphere of MONGE will be reduced to a point-sphere when S^2 is a cone ($\mathcal{L} = 0$) or into an equilateral hyperboloid if namely the equation

1) This ensues inter alia from

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{12} & a_{22} & a_{23} & a_{24} \\ a_{13} & a_{23} & a_{33} & a_{34} \\ a_{14} & a_{24} & a_{34} & a_{44} \end{vmatrix} \times \begin{vmatrix} A_{11} & A_{12} & A_{13} & A_{14} \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ A_{14} & A_{24} & A_{34} & A_{44} \end{vmatrix} = \begin{vmatrix} \mathcal{L} & a_{12} & a_{13} & 0 \\ 0 & a_{22} & a_{23} & 0 \\ 0 & a_{23} & a_{33} & 0 \\ 0 & a_{24} & a_{34} & \mathcal{L} \end{vmatrix}$$

(See a. o. BALTZER, Determinanten, 5th edition, p. 63).

$$(a_{11}a_{22} - a_{12}^2) + (a_{22}a_{33} - a_{23}^2) + (a_{33}a_{11} - a_{13}^2) = 0$$

is satisfied.

In the latter case the asymptotic cone possesses as is known ∞^1 triplets of mutually perpendicular tangent planes.

2. When in the equation

$$A_{11}(x^2 + y^2 + z^2) - 2(A_{11}x + A_{21}y + A_{31}z) + (A_{11} + A_{22} + A_{33}) = 0$$

we substitute $a_{ik} + \lambda b_{ik}$ for a_{ik} , the new equation represents the system of the spheres of MOXGE belonging to the quadratic surfaces of a pencil.

The equation is a cubic one in λ ; so the indicated spheres form a system with index 3, that is, through each point three spheres pass.

If for brevity's sake we represent the formula

$$x^2 + y^2 + p_k x + q_k y + r_k$$

by C_k , the cubic equation is

$$l_0 C_0 \lambda^3 + l_1 C_1 \lambda^2 + l_2 C_2 \lambda + l_3 C_3 = 0.$$

The power of a point with respect to the sphere (λ) is then equal to

$$\frac{l_0 C_0 \lambda^3 + l_1 C_1 \lambda^2 + l_2 C_2 \lambda + l_3 C_3}{l_0 \lambda^3 + l_1 \lambda^2 + l_2 \lambda + l_3}.$$

This expression becomes independent of λ for the centre of the sphere cutting the four spheres C_k orthogonally: *all the spheres of the indicated system are intersected at right angles by a fixed sphere.*

On this *orthogonal sphere* the point-spheres of the system are of course situated; so it contains in the first place the *vertices* of the four *cones*, in the second place the *centres* of the two *equilateral hyperboloids*¹⁾ belonging to the pencil.

From this ensues that the locus of the centres of the spheres is a skew cubic. This is moreover confirmed by the observation that in

$$x_0 = A_{11} : A_{44} \quad , \quad y_0 = A_{21} : A_{44} \quad , \quad z_0 = A_{31} : A_{44}$$

the numerators and the denominators are cubic forms in λ .

The square of the radius being represented by the quotient of two forms of order six in λ , the system contains six spheres with given radius.

3. The quadratic surface indicated by the equation in tangential coordinates ξ, η, ζ

1) Their parameters are determined by

$$\sum_3 [(a_{11} + b_{11} \lambda)(a_{22} + b_{22} \lambda) - (a_{12} + b_{12} \lambda)^2] = 0.$$

$$\sum_3 a_{11} \xi^2 + 2 \sum_3 a_{12} \xi \eta + 2 \sum_3 a_{13} \xi + a_{44} = 0$$

has for equation in point coordinates

$$\sum_3 A_{11} x^2 + 2 \sum_3 A_{12} x y + 2 \sum_3 A_{13} x + A_{44} = 0.$$

If now a_{ik} is the minor of the determinant $\sum \pm A_{11} A_{22} A_{33} A_{44}$, corresponding to A_{ik} , the sphere of MONGE of the indicated surface is represented by

$$a_{11} (x^2 + y^2 + z^2) - 2 (a_{11}x + a_{21}y + a_{31}z) + (a_{11} + a_{22} + a_{33}) = 0.$$

But we have ¹⁾ $a_{ik} = a_{ik} \Delta^2$; so this equation can be replaced by

$$a_{11} (x^2 + y^2 + z^2) - 2 (a_{11}x + a_{21}y + a_{31}z) + (a_{11} + a_{22} + a_{33}) = 0,$$

or by

$$\left(x - \frac{a_{11}}{a_{11}}\right)^2 + \left(y - \frac{a_{21}}{a_{11}}\right)^2 + \left(z - \frac{a_{31}}{a_{11}}\right)^2 = \frac{1}{a_{11}^2} \sum_3 (a_{22}^2 - a_{11} a_{44}).$$

So for a tangential pencil of quadratic surfaces we find

$$(a_{11} + b_{44} \lambda) (x^2 + y^2 + z^2) - 2 \sum_3 (a_{11} + b_{11} \lambda) x + \sum_3 (a_{11} + b_{11} \lambda) = 0,$$

that is, the corresponding spheres of MONGE form a pencil.

To this belong the point-spheres indicated by

$$\sum_3 [(a_{11} + b_{11} \lambda)^2 - (a_{11} + b_{11} \lambda) (a_{11} + b_{11} \lambda)] = 0,$$

originating from two equilateral hyperboloids, and the plane determined by $a_{11} + b_{44} \lambda = 0$ belonging to the paraboloid of the tangential pencil.

Physics. — “*The variability with the density of the quantity b of the equation of state.*” By Dr. J. D. VAN DER WAALS JR. Communicated by Prof. J. D. VAN DER WAALS.

§ 1. If we suppose the molecules of a gas ²⁾ to be perfectly smooth, elastic spheres, the influence of the fact that their diameter is not infinitely small, on the form of the equation of state may be allowed for in first approximation by diminishing the volume V , in which the gas is contained, with four times the volume of the molecules. If we understand by distance sphere a sphere described concentric with a molecule and with a radius 2σ (where σ denotes the

¹⁾ See inter alia BALTZER, l. c. p. 65.

²⁾ I say only “gas” not “gas or liquid”, for we must not apply the formula for a liquid without introducing still other approximated terms than those that will be discussed here.

radius of the molecule), then we may also say, that we must diminish V with half the combined volumes of the distance spheres, which quantity is usually denoted by b , or by b_{∞} if we wish to take into account the variability of the correction in consequence of variation in density. Various methods have been followed in order to investigate this influence; all these methods yielded a conformable result, so that no reasonable doubt can exist as to the correctness of this statement.

We should be inclined to deduce from this, that the influence may be correctly allowed for in second approximation by diminishing V with half the volume really occupied by the distance spheres, in which a segment which two distance spheres have in common, is counted only once, or what comes to the same, by writing $b_{\infty} - \Sigma S$ instead of b_{∞} , ΣS representing the sum of all the segments which are covered by two distance spheres at the same time. The correction has been introduced in this way by Prof. J. D. VAN DER WAALS ¹⁾; and Dr. J. J. VAN LAAR ²⁾ has made a calculation of a second correction term, which is based on a similar supposition. I will however confine myself to the discussion of the first correction term, for which we find in this way $\frac{17 b_{\infty}^2}{32 V}$. The question whether the first correction

term is correctly found in this way has not been answered un-animously in the affirmative. BOLTZMANN ³⁾ follows quite a different method for calculating it and finds $\frac{3 b_{\infty}^2}{8 V}$. Though BOLTZMANN in his communication in these Proceedings expressed the wish that his publication of this result differing from my father's would give rise to a discussion by which this doubtful point might be elucidated, no discussion has followed by which the question has been settled conclusively. Now I think I can show that there is no reason for

introducing the correction in the way which yields the value $\frac{17 b_{\infty}^2}{32 V}$ and at the same time I will give a reasoning, by which the term $\frac{3 b_{\infty}^2}{8 V}$ is derived in a shorter way than that followed by BOLTZMANN.

The simplest way to show clearly what supposition we must make in order to get the correction term $\frac{17 b_{\infty}^2}{32 V}$ is to start from the

¹⁾ Versl. Kon. Akad. v. Wetensch. V. p. 150. Oct. 1896.

²⁾ These Proceedings Vol. I, p. 273. Jan. 1899.

³⁾ These Proceedings Vol. I, p. 398. March 1899; and "Vorlesungen über Gastheorie" II, p. 151.

virial equation as my father has done for the external pressure and for the pressure of the molecular attraction in Chapter II of his "De Continuïteit van den Gas- en Vloeïstoftoestand" and for the forces eventuating in collisions of two molecules in these Proceedings Vol. I, p. 138. Oct. 1898.

First, however, I will point out, that the virial equation need not necessarily be applied for a definite quantity of matter, which is contained in a definite volume and enclosed within a solid wall, as is the usual method of applying it. We may as well apply that equation for a part of a homogeneous phase, separated by an imaginary separating surface from the surrounding substance which is in the same phase. We shall not always find *the same* molecules within such a surface, but we may assume, that at two different instants t_1 and t_2 we shall find *the same number* or at least with very great approximation the same number of molecules within it, and that the expression $\sum m \dot{x} \frac{dx}{dt}$ will also have the same value at the instants t_1 and t_2 . We may therefore put:

$$\frac{d}{dt} \sum m \dot{x} \frac{dx}{dt} = 0$$

and also the corresponding equations for the y - and for the z -coordinate.

From this we may deduce:

$$\sum m s^2 = - \sum \left[x \frac{d m \dot{x}}{dt} + y \frac{d m \dot{y}}{dt} + z \frac{d m \dot{z}}{dt} \right] (A)$$

In the case that we may neglect the volume of the molecules with regard to the volume in which they are contained, and that we may assume that the molecular forces act in such a way that they yield on average zero for the force exercised on a molecule within a homogeneous phase, the righthand member of this equation has only a value at the border of the volume under consideration: it may therefore be reduced to a surface-integral.

The lefthand member of this equation is independent of the circumstance whether the space under consideration is enclosed within an imaginary separating surface or within a solid wall, and in the latter case it is also quite independent of the properties of this wall. So the righthand member cannot depend upon these circumstances either. In the case of a solid wall we may write: $\frac{dm}{dt} = 0$. So we get for the righthand member:

$$-\int P' r \cos(n, r) do = 3 P' V \dots \dots \dots (B)$$

Here r represents the radius vector drawn from the origin of the system of coordinates to a point of the surface, do represents an element of that surface, $\cos(n, r)$ the cosine of the angle which the radius vector forms with the normal to the surface. P' is the force per unit of surface which prevents the molecules to leave the space and compels them to return towards the inside of it. We may distinguish in it the molecular pressure $\frac{a}{n^2}$ and the pressure p exercised by the wall.

For the case of an imaginary separating surface, $\frac{d}{dt} m \frac{dx}{dt}$ is the momentum in the direction of the positive x -axis conveyed through the surface to the inside of it. Momentum conveyed to the outside has to be taken into account with the negative sign. In this case also the righthand member may be represented by equation (B) though here the symbol P' does not any longer represent a force which really acts on the molecules.

In the case that the volume really occupied by the molecules is not so small that we may neglect it, also the virial of the forces eventuating in the mutual collisions of the molecules must be taken into account. If we denote this virial by I then we may write equation (A) in the following form:

$$\Sigma ms^2 = -I - \int Pr \cos(n, r) do = -I + 3 PV.$$

Σms^2 and I being independent of the properties of the bordering surface, P cannot depend upon them either. P appears to be greater than P' : for a wall this is because the number of collisions is augmented in consequence of the abbreviation of the mean length of path which a molecule describes between two successive collisions; for an imaginary separating surface this is because the conveyance of momentum through that surface has augmented in consequence of the fact that in collisions between two molecules whose centers lie at opposite sides of the separating surface, the momentum is transplaccd instantaneously from the center of one molecule to that of the other; so the momentum has been transported with infinite velocity.

But the way in which we have derived the quantity P which may be estimated to represent the pressure prevailing in the gaseous or in the liquid phase, warrants in any case that this quantity is

independent of the shape of the vessel and the properties of the walls in which the phase is enclosed, but on the other hand it warrants also that we may find the quantity P by calculating the pressure which would be exercised against a plane wall if the molecules did not attract one another, or by adding $\frac{a}{r^2}$ to the pressure exercised by mutually attracting molecules against a plane wall.

The way in which the virial of the forces eventuating in mutual collisions of the molecules has been introduced by Prof. VAN DER WAALS is as follows. We assume that in first approximation P represents also the pressure exercised on the distance spheres of the molecules. This would yield the value $2Pb_\infty$ for the virial. We must, however, take only half this value, else all the forces would have been counted twice.

The distance spheres, however, cannot be considered as unmovable solid walls, but as moving and movable walls and therefore it is perhaps not quite superfluous to show expressly that they are indeed subjected to a pressure amounting in first approximation on average to P . I will give the proof of this proposition in § 2 of this communication.

The introduction of the correction term $\frac{17}{32} \frac{b_\infty^2}{V}$ is based on the consideration that the value of the virial given above will be too great because some of the distance spheres partly coincide. The parts of the surface of a distance sphere I falling within a distance sphere II are protected from collisions with all other molecules but II. Therefore the pressure on such parts is assumed to be zero; on the other parts the pressure on the distance spheres is supposed to be P . This comes to the same as the assumption that the average pressure during a time τ (and every pressure which we consider, the pressure P also, cannot be anything else but an average value during a certain time τ) exercised on an element do of a distance sphere would be smaller than P , because of the fact that the element do is only during a part of the time τ exposed to the pressure P , during another part of that time, however, it would have been subjected to no pressure, because it was protected by the distance sphere of a molecule II from collisions with other molecules.

I have two objections to the calculations based on these considerations.

In the first place the assumption is made, that a part of a distance sphere would never experience any pressure, when it lies within the distance sphere of another molecule. In fact the reverse is true: in order that a surface element should experience a pressure, a

molecule must collide against it and then it lies in the distance sphere of that molecule; and the considerations in which the pressure inside the distance spheres is assumed to be zero, outside them to be P , are certainly not a correct representation of what really happens. Yet points lying inside distance spheres are in somewhat different conditions as to the pressure that may be exercised on them, than points outside distance spheres. It is not clear to me how these conditions should be taken into account. It is, however, not necessary to know this in order to calculate the correction term, as will appear from my second objection.

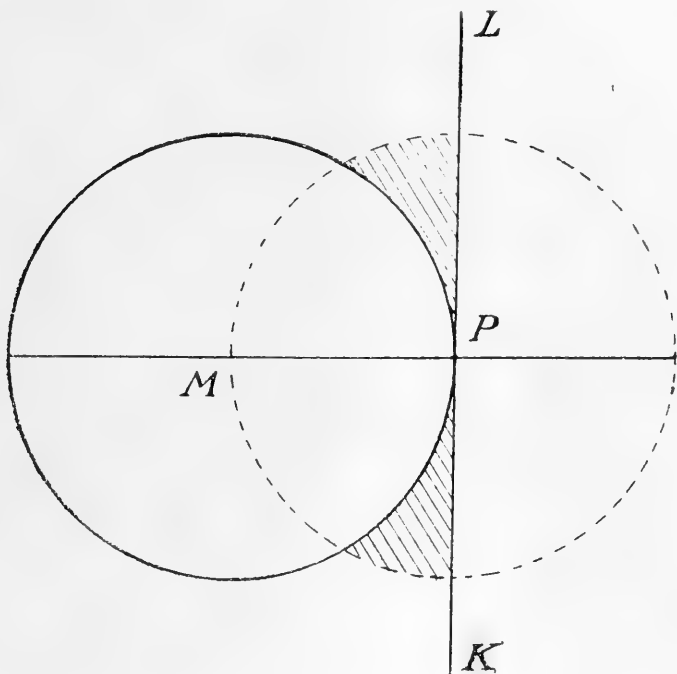
In the second place the fact has been overlooked that not only some parts of distance spheres lie within other distance spheres but that the same circumstance occurs for parts of the bordering surface. It is indifferent whether this is an imaginary surface or a solid wall¹⁾, in any case a part of it will lie within the distance spheres of the molecules, and may therefore with as much (or as little) right be estimated to be protected from pressure. Now let $1/\lambda$ part of the bordering surface lie within the distance spheres. If we must assume that this part of the surface experiences a pressure zero, and that the free surface experiences a certain pressure, that we will call P_1 , then the quantity P , which represents — as appears from the way in which it has been introduced — the average pressure, would be equal to $\frac{\lambda-1}{\lambda} P_1$. Let us now investigate what part of the total surface of the distance spheres lies within other distance spheres, and let $1/\lambda_1$ represent that fraction, then the average pressure of a distance sphere will amount to $\frac{\lambda_1-1}{\lambda_1} P_1$. If λ_1 were equal to λ , then the average pressure on the bordering surface and on the distance spheres would be the same, and we should not have to apply any correction to the term b_∞ .

We find the correction term $\frac{17b^2}{32V}$ if we make the following assumption, but only in that case: every surface element, — no matter whether it is a part of a solid wall or of an imaginary separating surface, and whether the surface is plane or curved and no matter whether it lies within or without the distance spheres of molecules —

1) The virial of the forces exercised by the wall must properly not be integrated over the wall itself, but over the surface which contains the centers of the molecules colliding against the wall, i. e. over a surface parallel to the wall and lying at a distance σ from it.

it will always experience a pressure P . Only the distance spheres make an exception to this rule, for parts of them, falling within other distance spheres experience a pressure zero.

I can find no reason for this exception and therefore I think the value $\frac{17}{32} \frac{b_{\infty}^2}{V}$ incorrect. The question whether in fact a correction must be applied depends on the fact whether λ_1 is equal to λ or not. This may be investigated in the following manner.



Let M in the figure represent the center of a molecule and let the circle described with M as center, represent the section of the distance sphere (I) of that molecule with the paper. Now we are to calculate the average pressure exercised during a time τ on a surface element db , the center of which we call the point P . To this purpose we describe a circle II with P as center and with a radius 2σ and we also consider the tangent plane in P which we call LK .

Two cases may be distinguished:

1st The space within sphere II but outside sphere I and at the left of the tangent plane (the section of the space in question with the paper has been hatched in the figure) may contain the center of a molecule; if this is the case P lies within the distance sphere of that molecule.

2nd The space under consideration may not contain the center of any molecule.

We will call that part of the time τ during which the former takes place $\frac{\tau}{\mu}$; so that part during which the latter takes place $\frac{\mu-1}{\mu}\tau$. During the time $\frac{\mu-1}{\mu}\tau$ the surface element do is quite in the same circumstances as an element of a plane wall. Therefore it will experience on average a pressure P . This pressure P is a quantity which we may derive from the virial equation; in order to determine it, it is therefore not required to decide whether the considerations in consequence of which we find P equal to $\frac{\lambda-1}{2}P_1$ are correct or not. But when the former case takes place, so during the time $\frac{\tau}{\mu}$, we are certainly justified in assuming that do does not experience any pressure. The average pressure on do is therefore $\frac{\mu-1}{\mu}P$.

We may find the value of μ in first approximation by determining the volume v of the hatched space, and by assuming that the chance that a certain definite molecule will lie within that volume is equal to $\frac{v}{V}$. If n denotes the total number of molecules, then the chance that the space contains a molecule will be represented by $n \frac{v}{V}$. On average the value of $1/\mu$ will be equal to this chance; therefore in first approximation $1/\mu = n \frac{v}{V}$.

We find by a simple calculation for v the value $\frac{1}{4}\pi r^3$, where $r = 2\sigma =$ the radius of a distance sphere. Therefore:

$$1/\mu = n \frac{\frac{1}{4}\pi r^3}{V} = \frac{3}{8} \frac{b_\infty}{V}.$$

The internal virial I will therefore be $3Pb_\infty \left(1 - \frac{3}{8} \frac{b_\infty}{V}\right)$ and equation (1) assumes the following shape:

$$1/3 \sum m s^2 = P V - P b_\infty \left(1 - \frac{3}{8} \frac{b_\infty}{V}\right) = P \left(V - b_\infty + \frac{3}{8} \frac{b_\infty^2}{V}\right).$$

§ 2. In order to introduce the internal virial I I started from the supposition that the distance spheres of the molecules experience a pressure which is on average equal to P . As I never found a direct proof of this thesis I will give it here. The pressure P namely may i. a. be considered to represent the pressure exercised against a solid unmovable wall, disregarding the molecular pressure. The distance spheres, however, are not to be regarded as a solid, unmovable wall. In consequence of their motion the number of collisions against a surface element do of a distance sphere is greater than that on an equal element of the wall; moreover the force in each collision is proportional to the relative velocity of the molecules, which is greater than the velocity of each molecule separately.

From these two circumstances we are apt to assume that the average pressure on the distance spheres would be greater than P .

On the other hand the impulse of a molecule colliding with a velocity s normally against a solid, unmovable wall is $2ms$. If, however, the molecule collides with the velocity s centrally against another unmovable molecule with the same mass, then the first molecule will be stopped and the second will obtain the velocity s ; so the impulse is in this case only ms .

In consequence of this circumstance we should be inclined to expect the pressure on a distance sphere to be smaller than P .

The following simple calculation will suffice to show that these influences cancel each other and that the pressure exercised on the distance spheres is really equal to P , at least in the case that we may neglect the volume of the molecules with regard to the volume in which they are contained.

Let us imagine two molecules I and II with the same mass. The same proposition might be proved without difficulty also for mixtures, so for molecules with unequal masses, but I will confine myself here to molecules with the same mass. The velocities of the molecules will be denoted by s and s_1 and the components of these velocities by u, v, w and u_1, v_1, w_1 . The chance that molecules occur whose velocities have these components will be represented by $F(u, v, w)$ and $F(u_1, v_1, w_1)$ and the relative velocity by s_r . Then we have:

$$s_r^2 = (u-u_1)^2 + (v-v_1)^2 + (w-w_1)^2.$$

If we take the direction of s_r as the axis of a system of spherical coordinates, and if we call the latitude φ the longitude ψ , then a surface element of the distance sphere of molecule I will be represented by $r^2 \sin \varphi d\varphi d\psi$. The number of collisions per unit of time of molecules of group II against such a surface element is:

$$F(u, v, w) F(u_1, v_1, w_1) du dv dw du_1 dv_1 dw_1 s_r r^2 \sin \varphi \cos \varphi d\varphi d\psi.$$

Not the total relative velocity s_r changes its sign in a collision of this kind, but only the component normal to the tangent plane in the point in which the molecules touch one another. The impulse is therefore $m s_r \cos \varphi$.

The total impulse of the collisions of the kind under consideration will therefore be equal to:

$$F(u, v, w) F(u_1, v_1, w_1) du dr dw du_1 dv_1 dw_1 s_r^2 r^2 \sin \varphi \cos^2 \varphi d\varphi d\psi.$$

The eightfold integral of this expression yields the total pressure exercised on the surface of the distance spheres. We have:

$$\iint r^2 \sin \varphi \cos^2 \varphi d\varphi d\psi = \frac{2}{3} \pi r^2$$

if we integrate according to ψ between the limits 0 and 2π and according to φ between the limits 0 and $\frac{1}{2}\pi$. The limits for φ are not 0 and π , for the parts of the distance sphere of molecule I for which $\varphi > \frac{1}{2}\pi$, cannot come into collision for the given relative velocity s_r . We may write $s^2 + s_1^2$, for s_r^2 for the terms $s s_1 \cos(s, s_1)$ yield zero on average. Doing this we may integrate the term with s^2 according to du_1 , dv_1 and dw_1 ; so we get:

$$\int F(u_1, v_1, w_1) du_1 dv_1 dw_1 = n.$$

The term with s_1^2 on the other hand may be integrated according to du , dv and dw ; so we get:

$$\int F(u, v, w) du dv dw = n.$$

This yields for the total pressure on the surface of the distance spheres:

$$\frac{2}{3} \pi r^2 n \left[\int m s^2 F(u, v, w) du dv dw + \int m s_1^2 F(u_1, v_1, w_1) du_1 dv_1 dw_1 \right].$$

Both integrals in this expression are equal to $n m s^2$, $m s^2$ representing twice the mean kinetic energy of a molecule. We may therefore write this expression as follows:

$$\frac{4}{3} \pi r^2 n^2 m s^2.$$

Dividing this quantity by the total surface of the distance spheres $4\pi r^2 n$, we get for the value of the average pressure:

$$\frac{1}{3} n m s^2.$$

This is the same value as we find for the pressure exercised on a solid, unmovable wall.

In order to calculate the number of collisions we have here neglected the extension of the molecule and the mutual attraction of the molecules. Therefore it is apparent that we cannot have obtained anything else but a first approximation.

Botanics. — “*Die Stele-Theorie*”. Dissertation of Mr. J. C. SCHOTTE.
(Communication of Prof. J. W. MOLL).

According to the idea of VAN TIEGHEM, given about the tissues of root and stem of the vascular plants, they must be divided into three groups or systems of tissues, namely, epidermis, cortex and central-cylinder. It is such a natural thing to call the epidermis a separate tissue that already a long time before VAN TIEGHEM, it was acknowledged and is at present generally accepted.

It is a different thing about the theory that the central part of stem and root is taken up by a cylinder of tissue, the central-cylinder (or “*stèle*”), which may consist of elements differing greatly, but which must nevertheless be regarded as a connected whole, forming a certain contrast with respect to the cortex. This consideration which can be called the “*Stelar-theory*” is accepted by some, rejected by others. It is of the greatest importance for instruction and for the construction of descriptions of the inner structure, and it has undoubtedly for both these reasons such a great practical weight, that for this reason only it deserves our attention in a high degree. The scientific foundations for this theory are not in such a good condition and assuredly its non-acceptance is owing to this. Of course the important question is, whether this distinction between cortex and central-cylinder has made its appearance already at an early period in the phylogeny of plants. With the present state of our knowledge this can perhaps not be proved with certainty; but to be able to answer this question in the affirmative two conditions must be put: 1st. the central-cylinder must be indicated if not in all, still in the greater part of stems and roots, 2nd. it must appear already at an early period in the development of these organs.

As for the root these conditions are amply satisfied, which gives great support to the theory of VAN TIEGHEM. But this is not the case to such an extent for the stem, partly perhaps in connection with the complications formed already at an early period by the develop-

ment of the leaves, partly in connection with the splitting up of the central-cylinder in these organs of many plants. Concerning the latter point VAN TIEGHEM himself and of late a number of American and English investigators: GWYNNE-VAUGHAN, JEFFREY, BOODLE, FAULL, WORSDELL, BRETELAND FARMER & HILL, Miss FARD, TANSLEY & LULHAM, BREBNER have shed much light. In all those cases in which stems show a number of loose strings, regarded by some as parts of a central-cylinder (schizostely), by others as vascular bundles, a single central-cylinder, the monostelic structure, is rule in the youngest internodes of the plant, in hypo- and epicotyl and in the internodes following immediately.

But in most cases there is no question about schizostely and so according to VAN TIEGHEM we must expect monostely. However it is a fact, that whilst in every root the most superficial microscopic investigation easily proves the existence of a central-cylinder, this is not at all the case for many stems. The inner layer of the cortex (endodermis), it is true, is often developed as a bundle-sheath indicating as that of the root does, the boundary of the central-cylinder, or also it contains starch-grains, so that a distinct starch-sheath is formed; but in a great many other cases, also in an investigation made for that purpose, as was done by H. FISCHER, it has not been possible to point out a well defined central-cylinder. FISCHER found in 100 investigated plants only in 32 cases a distinct endodermis.

It has now been shown by Mr. SCHOUTE that this objection to the Stellar-theory does not exist in reality. He collected out of the literature on this subject numbers of cases, in which a distinct endodermis had been observed in some shape or other. He himself studied a great number of stems of different plants and then it was evident how necessary it is to examine these organs in different and especially in young stages of their development, a thing FISCHER had not done. The result of this method of working was, that of about 400 dicotyledonous plants only in 7 no distinct endodermis was come across and among these 7 there were yet 4 which even showed a sharp boundary of the central-cylinder. Also the greater part of the Monocotyledonous plants possess an endodermis. It is not to be found in Gymnosperms but yet here as is the case in most of the above-mentioned exceptions, a distinct boundary between cortex and central-cylinder is often to be seen. So this result is very favourable for the Stellar-theory and is a contribution to its scientific confirmation.

But in yet another manner has Mr. SCHOUTE endeavoured to test the Stellar-theory, a test, which it is true has led to a negative result, but which enables us to draw weighty conclusions with regard to

the value of the well known Theory of the histogens of HANSTEIN.

In working out his theory VAN TIEGHEM purposely avoided as much as possible to make use of the history of development, and as has been proved justly. Yet it was quite natural to think that there was a connection between the structure of the full-grown stem and root and that of the same organs at a very early period of development, in embryo or growing point. For HANSTEIN had established a doctrine about the structure of the meristems, very much like VAN TIEGHEM's theory and had gained a number of adherents. He thought, especially on account of the arrangement of the otherwise equivalent cells, to be able to distinguish three tissues in those meristems, called dermatogen, periblem and plerome. The last was a column of cells in the middle part of the stem and root. Of course it was quite natural to think of an identity of dermatogen and epidermis, periblem and cortex, plerome and central-cylinder, in such a manner that the latter had developed out of the former. If it were possible to point out such a correspondence, this would be for the Stellar-theory as well as for the Theory of the histogens of great importance, though not of equal importance for both. If the central-cylinder is already found in the meristem as an independent whole, this points to the fact, that the differentiation of this tissue is old and then the Stellar-theory has gained another support. But as I said above, it is fully established in another way and can very well do without this support.

The HANSTEIN-theory of the histogens is a different case. Every one who studies the literature impartially, will have to own that this doctrine rests on a very weak foundation, perhaps not with respect to the dermatogen, but very certainly as far as the plerome is concerned. It is true, there are some roots and a very few stems in whose thin tops the cells are arranged in a remarkably regular order, so that a central-cylinder can be distinguished as plerome. But in many roots and in nearly all stems there is no question about tracing such an arrangement up to the growing-point. It is really to be wondered at that this HANSTEIN-theory in its generality has found so many genuine adherents; this is certainly partly owing to the conviction, expressed by many and silently shared by others, that plerome and central-cylinder are one and the same.

Yet this had never been accurately examined till it was undertaken by Mr. SCHOUTE. But it is clear, that a positive result would be of the greatest importance for this theory. For there is no sense in accepting histogens without full-grown tissues corresponding to them. Moreover might be expected of a positive result the possibility of finding an undoubted plerome when following the boundary of

the central-cylinder upwards, also in those cases in which up till now the efforts had not been successful, perhaps on account of the great number of cells.

The investigation of Mr. SCHOUTE was an accurate comparative study of connected series of cross and lengthwise sections. It would lead me too far if I were to speak of this more in particulars. But in general the investigation was conducted in such a way that an attempt was made to pursue in the direction of the growing point the boundary between the series of cells which could be distinguished as endodermis and central-cylinder in the older parts. The results were in short as follows.

Of the root of *Hyacinthus orientalis* and *Linum usitatissimum* the series of cells of the endodermis and the outer layer of the central-cylinder (pericycle) were successfully and uninterruptedly pursued up to the growing-point. In these cases a cylinder of tissue could be distinguished in the top, which could quite naturally be compared to the plerome of HANSTEIN and which corresponded exactly to the later central-cylinder. Also in *Helianthus annuus* in the main the same was found, though the plerome did not appear here as a complex of cells closed at the top. In the stem of *Hippurus vulgaris*, one of the few stems in which different investigators have distinguished a plerome, this was not only successfully found back, but also the series of cells of endodermis and pericycle could be pursued uninterruptedly to the growing-point. However the cells of the plerome proved to form not only the central-cylinder but also the endodermis and two layers of cells of the cortex, so that the required correspondence did not exist here. In the stem of *Elodea canadensis* an uncertain result was obtained, as here a starch-sheath and a bundle-sheath were found, and it was not possible to make out which of the two must be regarded as endodermis. But in the root of *Ficaria ranunculoides* and in the stalks of *Aesculus Hippocastanum*, *Lysimachia Ephemenum*, *Eronimus europaeus* and *Ajuga reptans* an important negative result was obtained. Here it was perfectly evident that the series of cells of endodermis and pericycle cannot be pursued up to the top, but that they very soon stop short and are replaced by shorter series of cells not exactly in their prolongation and which in their turn soon undergo the same fate. In other words in all these cases the expectation was not only disappointed that in this way in difficult cases a plerome was to be found, but it was also irrefutably established that it does not exist here.

After the above-mentioned explanations it need not be demonstrated that these results as a whole must be regarded as fatal to the Theory

of the histogens. That in some selected roots there is some correspondence, makes no difference. That in slender tops built up out of relatively few, lengthwise series of cells a regular arrangement of cells may appear as was described above, is the most natural thing in the world. To give a particular explanation of this is unnecessary, and in no case are these single indications sufficient to establish solely on them a theory of histogens as that of HANSTEIN. And yet this would have to be done if one wished to adhere to this theory, for all other facts plead strongly against it. *Hippuris*, almost the only plant showing a plerome in the stem, has a structure altogether opposed to the theory. And the irregularly built tops form without doubt the overpowering majority.

It seems to me that by the investigation of Mr. SCHOUTE the Histogen theory of HANSTEIN is proved to be erroneous. A conclusion of somewhat general importance can still be deduced from these investigations. Many botanists think that to the cell-division in meristems a certain phylogenetic importance must be given, somewhat comparable to that of the germinal layers in zoology. But here is forgotten that in zoology in the history of development folds and again folds are spoken of, to a certain extent also histological differentiation is mentioned, but little or nothing of directions of cell-division or of arrangements of otherwise entirely equivalent cells. If the zoologist attains at beautiful results by the study of the history of development, it in nowise ensues from this that the study of the arrangement of cells in meristems will be able to furnish these. Rather will the botanist have to expect such explanations from the study of the development of outer forms, and of inner differentiations as a result of differences in the nature of cells. Experience has taught us that this expectation has a right to exist. But the Histogen-theory has certainly contributed to nourish the above mentioned wrong opinion. Now that this has been proved to be incorrect we may expect that the historic and phylogenetic importance which has often been ascribed to the divisions and arrangements of nondifferentiated and perfectly equivalent meristem-cells will be reduced to its right and very slight proportion.

Groningen, Jan. 29, 1903.

Physics. — “*Methods and apparatus used in the cryogenic laboratory. III. Baths of very uniform and constant low temperatures in the cryostat.*” Communication N°. 83 from the physical laboratory at Leiden by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of December 27, 1902.)

§ 1. By means of the cryostat described in § 8, Comm. 14. Dec. '94, and § 3, Comm. 51. Sept. '99 we can obtain a bath of liquefied gas which is shut off from the atmosphere and boils at ordinary or diminished pressure. In such a bath the temperature is sufficiently uniform and constant for many experiments and measurements. If we use almost pure gases and if the evaporated gas is regularly recondensed by means of a compression apparatus, which as described in Comms. 14. Dec. '94, 53. Sept. '99 and 54. Jan. '00, does not contaminate the gas, the bath may be maintained as long as we wish. The operations in the bath itself as well as the addition of the liquefied gas can be watched through the observing glasses. Vacuum glasses are not required so that similar cryostats may be constructed for measuring apparatus of any dimensions. Before long we shall describe a cryostat where the gas apparatus and the bath are more independent.

I was led to describe the form of the cryostat, as it occurs in Comm. 51, through the communication of the results for the dielectric constants of liquid gases. (Comm. 52 Oct. '99), for which measurements only the temperatures of -90° C. or -182° C. were required. For other measurements, however, a measuring apparatus, once immersed in the cryostat, has been used at the whole range of temperatures between, -23° C. (boiling point of methyl chloride at ordinary pressure) and -210° C. (nitrogen at reduced pressure), given by methylchloride nitrous-oxide, ethylene, methane, oxygen and nitrogen as they were successively admitted into the cryostat.

For a long time improvements have been made in this cryostat by means of which we can attain a much greater uniformity and constancy in the temperature, while retaining the afore-mentioned advantages. A description of these alterations has now become necessary in order to judge of the accuracy of the temperature readings in the results from various measurements where we have availed ourselves of these improvements. These measurements will be treated in the next communications. Among others I mention here those bearing upon the isothermals of diatomic gases (Comms. 69 March '01

and 78, March '02) and the comparison between the platinum resistance thermometer and the hydrogen thermometer (Comm. 77 Febr. '02) In this description, as in Comm. 51. Sept. '99, it seems to me desirable to illustrate the use of the cryostat by means of a special example. We will consider the comparison of the hydrogen thermometer with the resistance thermometer where also a thermo-element had been immersed in the bath.

Plate I shows the cryostat and some of the auxiliary apparatus to scale, the connections are represented schematically. It has been drawn on a smaller scale than plate I of Comm. 51 Sept. '99, (which should be consulted together with the one now given) but it will suffice to give a survey of the whole arrangement and to show some of the alterations. While the details of the unmodified parts can be studied on plate I of Comm. 51, plate II of the present Communication shows the details of the parts enclosed by the dot-dash-line of plate I, as far as they are required for consideration of the new arrangements. The connection of the apparatus shown in Pl. I with the gas circulation can be seen in Pl. IV Comm. 51. The comparison of the platinum thermometer p and the hydrogen thermometer T_h and their connections to the other pieces of the apparatus are given in Comm. 77 Febr. '02 § 3. For the comparison of the thermo-element Θ I am as yet obliged to refer to the very rough diagram of 1896 (Pl. I of Comm. 27 Mai and June '96). The communication, however, of some results for which the temperatures have been determined by means of a thermo-element will soon call for a description of the recent considerable improvements in the use of the thermo-elements.

On plates I and II a correction thermometer ξ , which is entirely independent of the cryostat, will be seen besides the three measuring apparatus mentioned above. It serves in our case to indicate the mean temperature of the capillary of the hydrogen thermometer, or in general, the mean temperature of similar pieces of measuring apparatus occupying the same part of the cryostat. For this purpose two spirals of platinum wire are wound round a glass rod, the one for that part of the rod, where the temperature varies slowly ξ_2 , the other for that part where the temperature varies rapidly ξ_1 . By means of the leads ξ_{00} , connected to the places of contact ξ_{11} , ξ_{12} and ξ_{21} and emerging through the tube ξ_{01} , we can determine the resistance of these spirals.

§ 2. First we shall mention some small changes in the cryostat of Comm. 51 which have no relation to the question of keeping the temperature constant and uniform.

The jet of liquefied gas let in at a (plate I) is directed, by means of the cock h_6 and the filter f , against a glass wall from which it streams along the delivery spout D_1 into the bath, here a double beaker $B_{01} B_{02}$ (Pls. I and II), placed in the beakers B_1, B_2, B_3 of Pl. I Comm. 51. The cock and filter form part of a cover which as described in Comm. 51, may be removed together with S_1 and S_3 from the cryostat and may also be replaced by a syphon or a capillary with a cock outside the cryostat. The spreading of the jet over the wall may be watched through the windows V_1 , and the height of the liquid in the bath through the windows V_2 . The filter f serves principally to prevent opaque dust from the lead (oxide of copper etc.) from depositing just at the place where the jet touches the glass. In many cases, however, it happened in spite of the care taken in purification, that the liquefied gas itself, while evaporating under reduced pressure in the cryostat, had deposited a substance, formerly dissolved in it but solid at the lower temperature, thus rendering the bath opaque. Therefore, differing from Comm. 51, a glass beaker C_1 (Pls. I and II) with numerous openings in the bottom C_{10} (Pl. II) and containing some glass wool was suspended by the regenerator spiral b (Pl. I Comm. 51). This filter may be lifted from the cryostat together with the piece S_6 .

With the arrangement as described in Comm. 51 all the gas, formed after the liquid leaves the cock, goes in the direction indicated by the arrows on Pl. I Comm. 51. With the arrangement as described here, however, the gas which is formed while the bath is being filled follows in the main a different direction to that which afterwards evaporates from the bath. In fact, differing from Comm. 51, a valve D_{110} with a spring D_{12} has been added, which almost closes the opening of the delivery spout D_1 for gas, but allows liquid to flow through a very narrow opening D_{111} along the gutter D_{13} . The first considerable quantities flowing from the cock, serve to cool all the beakers and the whole cryostat in the way indicated in Comm. 51 (the arrows of plate I might be borrowed from plate I of Comm. 51), unless the supply becomes so great that the valve D_{111} is opened and the gas also flows out through the opening R_{10} in the ring R_1 , plate II. The gas which later evaporates from the beaker B_{01} , finds the valve D_{111} closed and escapes only through the opening R_{10} , along the way indicated by the arrows on plate II, so that it serves only to screen the immediate neighbourhood of the bath from external heat.

The difference in form between the rings R_3 and R_4 on plate II and those on plate I Comm. 51 is very slight. This follows from the wish to use the parts that served in the experiments, referred to in

Comm. 51, as much as possible in the arrangement of the measuring apparatus considered here. Formerly the bath could be excentrically mounted with reference to the tube F_1 whereas this time a central mounting was desirable. The existing dimensions of parts of the apparatus have also had the result that in the experiments described here the bath must be placed a little too high with regard to the observing glasses V_2 , which might easily have been avoided if we had been perfectly free in our construction.

The glass ring R_6 , not occurring in the arrangement of Comm. 51, serves still better to screen the bath from external heat. Like the other beakers and glass cylinders B_1 , B_2 , B_3 , B_4 , B_{01} , B_{02} , it is silvered inside and outside, leaving open, however, vertical strips nearly corresponding in width with the resistance thermometer p .

The conical rim B_{01} lies loose on the beaker B_{01} . When the liquid boils up, it streams back to B_{01} along the wall of the funnel; if, however, B_{01} is filled to the brim and more liquid is poured in, this superfluous liquid flows over into the beaker B_{02} , which also is filled before a measurement is made. If an intense cooling of the neighbourhood of the bath is required, the beakers B_1 , B_2 , B_3 must also be filled. It should be remembered, however, that if this is done, the evaporation at low pressure, as long as liquid remains in the outer beakers, requires a powerful vacuum pump.

The bath itself only evaporates slowly. Instead of the double beakers B_{01} B_{02} we might take a vacuum glass in order to diminish the evaporation as has sometimes been done (comp. § 3). But it is not always easy to obtain vacuum glasses of the required dimensions and internally finished with the accuracy necessary for the proper working of the stirring apparatus. Moreover one will not be inclined to immerse delicate measuring apparatus in the bath before one is sufficiently certain that the vacuum glass will not burst as such of greater dimensions sometimes do.

§ 3. To make clear the purpose of the arrangements to be described in the next sections, it seems to me that the following particularisations will be useful. First of all the temperature gradient in the bath. Even when the liquid boils regularly we find that in the lower layers, as a result of the hydrostatic pressure, the temperature exceeds that of the upper layers. If, as often happens with greatly diminished pressures when boiling is not produced artificially, only evaporation at the surface occurs instead of boiling, the temperature in the upper layers of the bath may fall considerably below that of the lower. If then the liquid suddenly boils up, which always happens whenever

we do not stir vigorously, an unexpected change takes place in the distribution of the temperature in the bath and hence in the temperature of any measuring apparatus placed in it. In measurements of the kind considered here, we cannot allow such irregularities and fluctuations in the temperature of the bath, either as to time or place.

Of the various methods of preventing this sudden ebullition, the simplest is the generation of small bubbles of gas by means of the heat of a short resistance (boiling thread). If, however, there are ignitable gases among those successively introduced into the apparatus and if consequently an explosive mixture with air might be formed, this method is not without danger.

To bring about ebullition a current of gas is often led through the liquid, which, however, has the disadvantage of contaminating the evaporated gas. To avoid this difficulty I have led through the bath a current of the gas itself. This means was applied for instance to avoid the retardation in boiling in the vacuum vessel mentioned at the end of § 2, and also in order to cause a strong stirring in the bath by means of the current of gasbubbles. But this means also presents many difficulties, mostly arising from condensation phenomena in the delivery tube, or higher temperature of the gasbubbles; I therefore, preferred, the arrangement as described in § 4.

If the cryostat is used as it was intended to be in Comm. 51, the requirements for very accurate measurements would not be fulfilled, even though a uniform temperature throughout the bath was attained. There still remains a systematic regular rise of the temperature, because the gas used is never perfectly pure and the more permanent part evaporates first. In cases where measuring apparatus require longer to adopt the temperature of the bath than the time in which the temperature changes the amount permitted by the accuracy of the observation, we cannot reach more accurate results without additional means.

§ 4. We now pass on to the description of the arrangements which form the subject of this communication. The uniform temperature in the bath is obtained by stirring. The stirring apparatus is placed concentrically to the bath, thus leaving room in the most profitable way for the measuring apparatus. From this space the stirring apparatus (as in Comm. 27 May and June '96 Pl. III) is separated by a protecting cylinder ξ_0 (comp. the figure to the left of plate I). The upper ring χ_{01} is provided with small valves χ_{04} covering openings of the same form. If the stirring apparatus moves in the cylindrical space between ξ_0 and B_{02} the valves shut up

during the upward movement and open during the downward movement. The upward movement is brought about by means of the thin wires χ_1 , the downward movement by the weight of the stirring apparatus itself which for this purpose is weighted with the heavy ring χ_{02} by means of the rods χ_{03} . As yet a more rapid motion of the stirring apparatus than this method affords has not been required; if wanted a construction with small rods instead of threads would be necessary. The valves are hinged on bent pins χ_{041} . The complete section of the stirrer to the right of plate II shows the valves shut, the section of χ_{01} at the top shows them open. When the stirring apparatus is moved up and down and the bubbles of vapour escape the movements of the valves resemble those of the fins of fishes.

It is very important that the up and down motion of the ring should be perfectly perpendicular and that the protecting cylinder ξ_1 and the beaker B_{02} should have a perfectly vertical position for, to make the valves work properly, only a narrow space can be left between the stirrer and the cylindrical walls. The cylinder ξ_0 is enclosed between two rings provided with grooves ξ_1 and ξ_2 , of which the upper is connected with the ring ξ_3 by means of glass tubes. Through the operation of the spring ξ_{31} and the arch ξ_{30} , this ring is pressed against the ring ξ_4 on to which the beaker B_{02} with a ground upper rim is fastened by means of cords. To this ring ξ_4 the hooks ξ_7 are also fastened, against which the upper rim of the beaker B_{01} is also pressed by means of cords. In this way a cylindrical space is reserved for the pumping motion of the stirrer.

In order to admit the measuring apparatus it was advisable to leave free the whole space offered by tube I'_1 , which is equal to that in the bath available for a measuring apparatus. To this end the threads χ_1 , formed of very thin silk cords enclosed in steel wire are led through 3 openings E'_{31} in the cover E of the bath and then over a pulley axis χ_2 with three grooves to a connecting piece χ_3 , which is moved by a single thread passing over the pulleys χ_4 and χ_5 . The cord must be moved from outside the case and the case must remain perfectly air-tight. This is obtained by passing the cord through an india rubber tube χ_{61} , which at χ_{60} fits hermetically on to the cover of the cryostat and in which the thread χ_{62} is also hermetically fixed. A thin steel wire is wound spirally round the india rubber tube. In this way the walls of the tube offer sufficient resistance to the atmospheric pressure to prevent them from collapsing when low pressure exists in the cryostat, while at the same time

they remain elastic enough to permit the movements of the cord. A regular up and down motion of the stirring apparatus is secured by the wheel χ_7 .

§ 5. A constant temperature is attained by continually adjusting the pressure, at which the liquid in the bath evaporates, to the indications of a resistance thermometer p placed concentrically in the bath. A sensitive thermometer forms an inherent part of the cryostat under consideration when it is to be used for very constant temperatures and the dimensions allowing a resistance thermometer to be introduced, the latter has been chosen as the most trustworthy. Its inner diameter controls the greatest cross section of the measuring apparatus which can be immersed in the bath, and therefore, as in our case, it must correspond to that of the tube F_1 . The construction of this thermometer has been described in detail by B. MEILINK (Comm. 77 Febr. '02) with a view to a comparison between it and the hydrogen thermometer referred to above. The leads pass through the openings R_{30} , R_{40} of the ebonite rings R_3 and R_4 , and then through the stopper into the tube T_{11} . On the plates I and II they are indicated by the same letters as on the plate of Comm. 77.

When the bath has reached the required temperature the galvanometer in the WHEATSTONE'S bridge, which serves to measure the resistance of p , is adjusted to zero by introducing suitable resistances. As soon as the deviations of the galvanometer make it necessary, a sign is given to the assistant, charged with the regulation of the pressure in the cryostat, who then raises or diminishes the pressure, whereby the temperature in the bath rises or falls. The great volume of the cryostat is here very useful in checking oscillations in pressure. The arrangements required for the regulation of pressure are shown in plate I, the separate pieces of apparatus to scale and the connections schematically. (Comp. Comm. 51 Sept. '99, pl. IV). The assistant uses the oil manometer X_0 , which is connected to the cryostat by X_1 and X_2 (comp. pl. II Comm. 51) and the cock X_{00} , the cock X_{01} being open. If we shut the cock X_{01} the motion of the oil enables us to very accurately watch the variations of the pressure in the cryostat by means of the difference between the pressure in it and of the quantity of gas temporarily shut off in the reservoir X_{02} . If through some cause or other the variations of pressure increase considerably, or if we want to stop the regulation, or to proceed to another pressure, the oil is prevented from running over by our opening the cock X_{01} . The pressure in the cryostat is varied by more or less opening the fine cocks Y_{43} and Y_{42} of the regulation

tube Y_{41} . Two cases are to be distinguished here. With operations at ordinary pressure it will be sufficient to adjust the cryostat at a pressure a little higher than that of the atmosphere and to either connect the cock Y_{42} with a gasholder *Gas.* or to disconnect them, as the occasion demands. As soon as the pressure passes a certain limit settled for the cryostat, the gas escapes from the cryostat through the large safety apparatus. For operations at reduced pressure, the cryostat, after the pressure has been sufficiently lowered by means of the exhaustpump of the circulation *Ech.* 1, is disconnected from the latter and connected by means of the cock Y_{43} to the exhaustpump *Ech.* 2., and is then reduced to a lower pressure. Obviously we can sometimes avail ourselves for this latter operation of the same exhaustpump as used with *Ech.* 1. The evaporation will proceed more gradually when a connection is made to a reservoir at reduced pressure *Vac.*, plate. If a reservoir of large volume is used we can even work without an exhaustpump, which may be valuable when it is necessary to avoid vibration for the measurements. Thus with the bath of nitrogen under diminished pressure the auxiliary compressor of Comm. 54 Jan. '00 plate VII was connected near *Ech.* 1 to the gaslead and the vessel of 5 m³ mentioned above (comp. Comm. 14 Dec. '94 § 10) served as vacuum reservoir, after being exhausted through Y_{36} and Y_{37} by means of a BURCKHARDT vacuum pump, connected to the gaslead at *Ech.* 2. This vacuum pump will be described later.

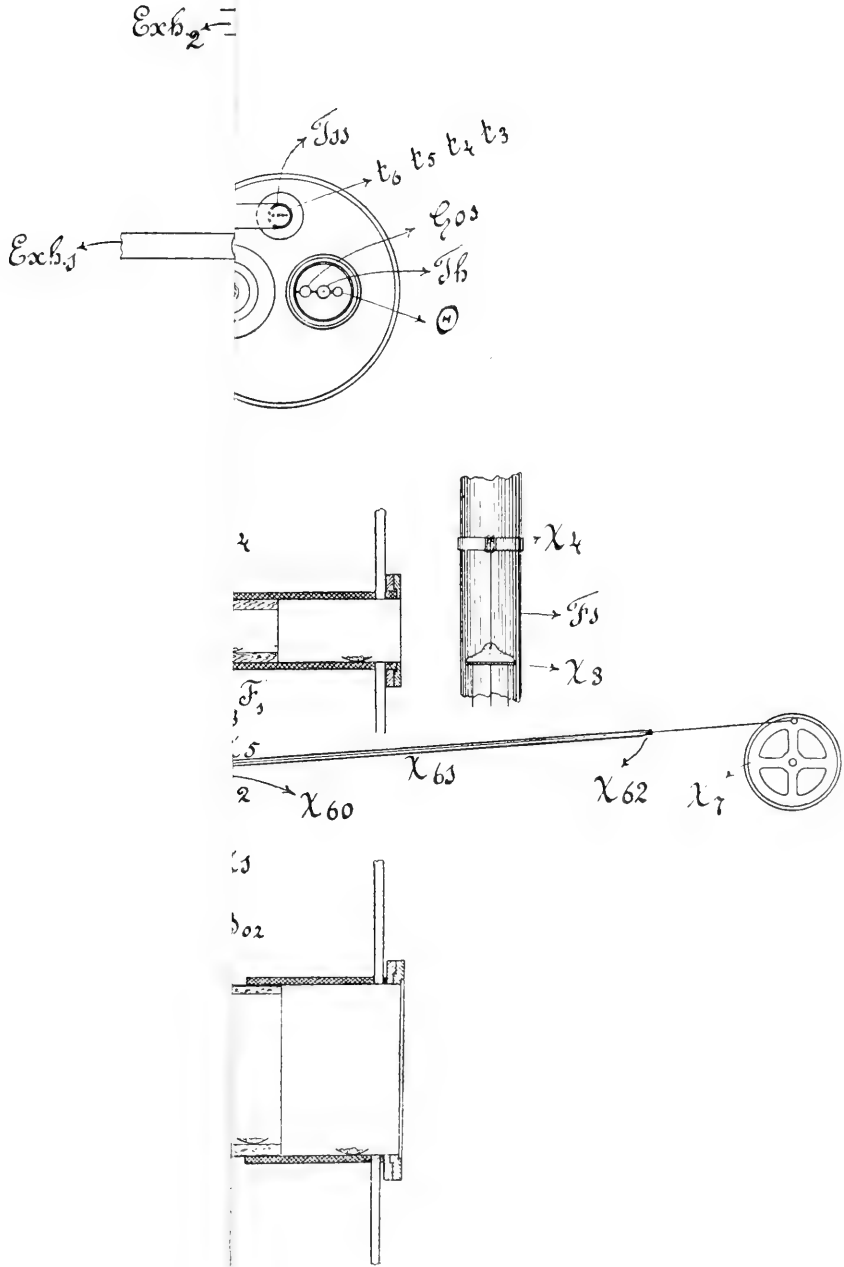
In a few words we shall indicate the method which we usually follow in order to get a wellfilled bath at diminished-pressure. First the double beaker B_{01} , B_{02} , or several beakers B_1 , B_2 , B_3 are filled at ordinary pressure, then we begin to slowly exhaust through Y_{34} ; all other cocks being shut by means of the pump, generally used for the circulation *Ech.* 1; while boiling is prevented by rapidly moving the stirring apparatus described in § 4. When the required pressure is reached the cryostat is to be connected to the great reservoir *Vac.* at the same pressure. If this cannot be done we hardly ever succeed in admitting through the cock h_6 the yet required quantity of liquid slowly enough to keep the pressure in the cryostat free from undesirably large fluctuations or even to avoid with the help of Y_{36} momentarily returning of it to nearly its ordinary value. Therefore, if a change of temperature for some time is allowed, it is in that case better to shut Y_{34} before more liquid is added and to connect the cryostat through Y_{35} to the gasholder. As long as the beaker B_{02} is not full the gas leaving the cryostat is allowed to pass through Y_{38} into the gasholder. If the beaker B_{02} is full, which is shown by

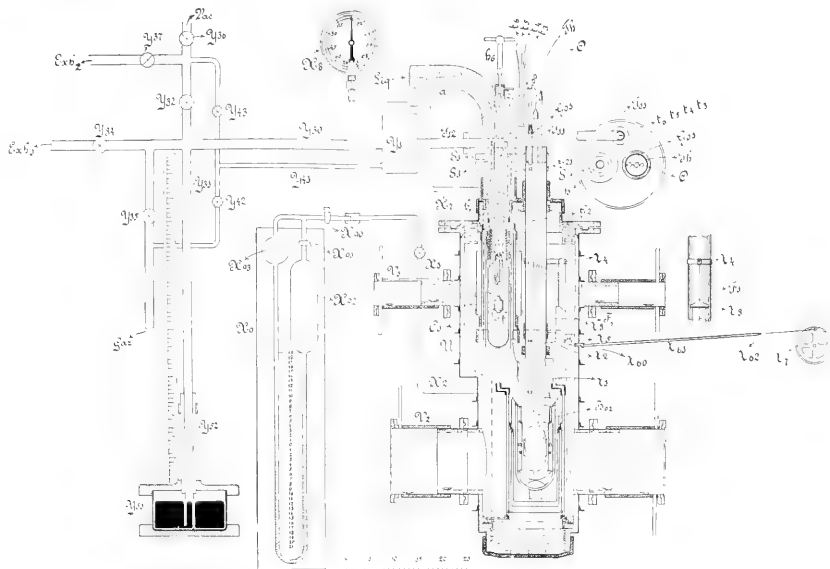
the rise of the level in B_{01} , we once more begin to diminish the pressure (Y_{32} shut, Y_{34} open) which process generally takes some time. Then more liquid is admitted as before and if necessary this process is repeated several times. If the beaker is sufficiently filled at the desired reduced pressure we begin to regulate the pressure with the duly exhausted vacuum reservoir as described above.

Plate III shows a couple of graphical representations of the variations of the temperature of the bath. The ordinates show the deflections on the scale of the galvanometer in centimeters. The abscissae represent the time in minutes; fig. 1 relates to a measurement in methane at ordinary pressure; a deflection on the scale of 1 c.m. corresponds to about 0.009 deg. (the open space in the figure indicates a magnetic disturbance). Fig. 2 refers to oxygen at a diminished pressure; here a deflection on the scale of 1 c.m. corresponds to 0.005 deg. They were borrowed from the measurements of MELLINK mentioned above.

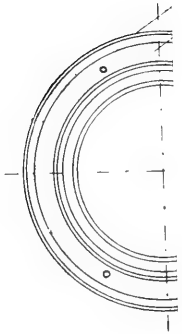
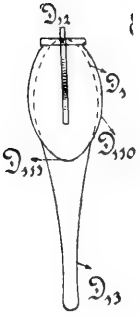
The temperature of the measurement is determined by the help of graphical representations, extending over the whole time of measurement, from which the portions reproduced on plate III have been taken. For this determination the readings of the galvanometer are noted down about twice every minute. By means of the planimeter we derive from the graphical representation obtained, the mean ordinate, which mean is considered as the temperature of the bath during the whole measurement.

(March 25, 1903).



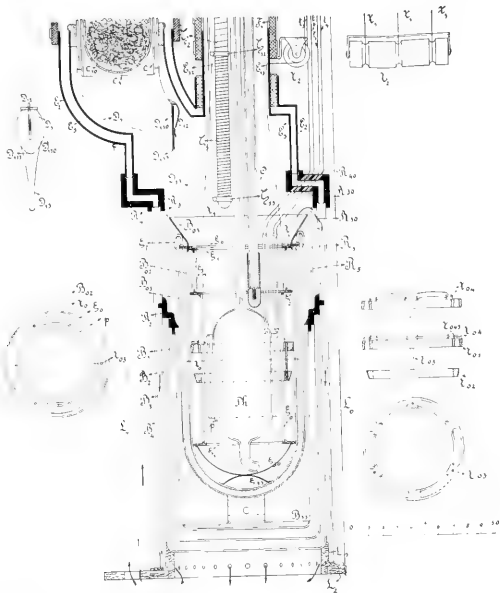


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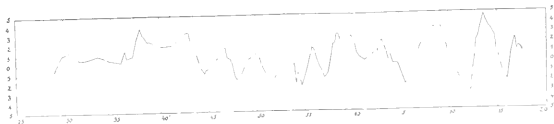
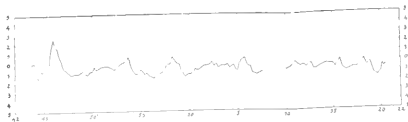
H. KAMERLINGH ONNES. Methods and apparatus used in the Cryogenic Laboratory. III Baths of very uniform and constant low temperatures in the cryostat.

PLATE II.



H. KAMERLINGH ONNES. Methods and apparatus used in the Cryogenic Laboratory. III. Baths of very uniform and constant low temperatures in the cryostat

PLATE III



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday March 28, 1903.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige
Afdeling van Zaterdag 28 Maart 1903, Dl. XI).

C O N T E N T S.

- J. J. VAN LAAR: "The meltingpoint-line of Tin-Amalgams" (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 511.
- A. W. NIEUWENHUIS: "Influence of changed conditions of life on the physical and psychical development of the population of Central Borneo", p. 525.
- P. H. SCHOUTE: "Relations between diagonals of parallelotopes", p. 540.
- E. COHEN and TH. STRENGERS: "On the atomic weight of Antimony (Communicated by Prof. W. H. JULIUS), p. 543, (with one plate).
- E. COHEN and C. A. LOBRY DE BRUYN: "The conductive power of hydrazine and of substances dissolved therein" (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 551.
- A. H. J. BELZER: "The velocity of transformation of tribromophenol bromine into tetrabromophenol" (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 556.
- J. H. BONNEMA: "Some new Under-Cambrian Erratic Blocks from the Dutch Diluvium (Communicated, by Prof. J. W. MOLL), p. 564.
- J. J. VAN LAAR: "On the course of the values of b for hydrogen, in connection with a recent formula of Prof. VAN DER WAALS." (Communicated by Prof. J. D. VAN DER WAALS), p. 573.
- W. H. JULIUS: "Peculiarities and changes of FRAUNHOFER-lines interpreted as consequences of anomalous dispersion of sunlight in the corona", p. 589.
- P. TESCH: "On the refractive index of rock-glasses" (Communicated by Prof. J. L. C. SCHROEDER VAN DER KOLK), p. 602, (with one plate).
- G. B. HOGENRAAD: "On an "Eisenrose" of the St. Gotthard". (Communicated by Prof. J. L. C. SCHROEDER VAN DER KOLK), p. 605.
- H. A. LORENTZ: "Contributions to the theory of electrons, I. p. 608.
- H. KAMERLINGH ONNES: "Methods and apparatus used in the cryogenic Laboratory". III (continued) IV, V. p. 628.
- H. KAMERLINGH ONNES and H. H. FRANCIS HYNDMAN: "Isotherms of diatomic gases and their binary mixtures. V. An accurate volumometer and mixing apparatus", p. 636, (with 2 plates)

The following papers were read:

Chemistry. — "*The meltingpoint-line of Tin-Amalgams.*" By
Dr. J. J. VAN LAAR. (Communicated by Prof. H. W. BAKHUIS
ROOZEBOOM). (2nd Communication).

(Communicated in the meeting of January 31, 1903).

1. In a previous communication (Proc. Dec. 1902) I showed, that when the molecular potential of tin in a liquid tin-amalgam is expressed by the formula

$$\mu_1 = f(T) + RT \log(1-x) + (\alpha_1 x^2 + \beta_1 x^3 + \dots),$$

a very good agreement is obtained between the *calculated* values of the melting-temperatures at various values of x , and the temperatures *observed* by VAN HETEREN (compare his Dissertation), at least up till about 80° C.

In a conference, I had since with prof. VAN DER WAALS, he called my attention to an expression for the correctionterm in μ_1 , which may be taken as a fairly good approximation¹⁾. This expression is:

$$\frac{\alpha_1 x^2}{(1 + vx)^2}.$$

After he had first shown (p. 193), that the correctionterm is really of the order x^2 — this I also showed in my previous communication, but in a different manner — and had observed, that (in the case investigated by him) the value of α_1 does not remain constant, but decreases when x increases (p. 198), he afterwards arrived at the said approximate expression (p. 213, 214), in agreement with an empirical relation of THOMSEN.

Though Prof. VAN DER WAALS has briefly given the deduction of his formula, it may be useful to state once more how this expression can be arrived at. The matter is of great importance, because the *same* quantity $\mu_1 - (\mu_1)_{x=0}$ constantly occurs in a great number of formulae, such as those for the lowering of the freezing-point, elevation of the boiling-point, alteration in vapour pressures, etc. If therefore this quantity is once for all accurately known, we may get a better insight into a great number of problems relating to binary mixtures.

2. As the *total* thermodynamic potential is represented by

$$\begin{aligned} \xi = & - \sum (n_1 k_1) T (\log T - 1) + \left[\sum (n_1 (e_1)_0) - T \sum (n_1 (\eta_1)_0) \right] - \\ & - \left[\int p dV - pV \right] + RT \sum (n_1 \log n_1), \end{aligned}$$

we obtain for the *molecular* potential of the component n_1 :

$$\mu_1 = \frac{\partial \xi}{\partial n_1} = -k_1 T (\log T - 1) + [(e_1)_0 - T(\eta_1)_0] - \left[\frac{\partial}{\partial n_1} \int p dV - p \frac{\partial V}{\partial n_1} \right] + RT + RT \log n_1.$$

With

$$p = \frac{\sum n_1 \cdot RT}{V - b} - \frac{a}{V^2}$$

¹⁾ Zeitschrift für Ph. Ch. 8, pg. 188 (1891). Also compare different passages in the second part of his "Continuität" on p. 43—45; 148; 152.

Recently, Prof. VAN DER WAALS has returned to this question in his "Ternary Systems" (Proc. March to July 1902). He gives there a more general and accurate expression, wherein occur the critical temperature and pressure of the mixture (Compare in particular IV, p. 92—96).

we find :

$$\int p dV = \sum n_1 \cdot RT \log (V-b) + \frac{a}{V},$$

and therefore

$$\frac{\partial}{\partial n_1} \int p dV = RT \log (V-b) + \frac{\sum n_1 \cdot RT}{V-b} \frac{\partial (V-b)}{\partial n_1} - \frac{a}{V^2} \frac{\partial V}{\partial n_1} + \frac{1}{V} \frac{\partial a}{\partial n_1}.$$

Deducting from this :

$$p \frac{\partial V}{\partial n_1} = \left[\frac{\sum n_1 \cdot RT}{V-b} - \frac{a}{V^2} \right] \frac{\partial V}{\partial n_1},$$

we get :

$$\frac{\partial}{\partial n_1} \int p dV - p \frac{\partial V}{\partial n_1} = RT \log (V-b) - \frac{\sum n_1 \cdot RT}{V-b} b_1 + \frac{2}{V} (n_1 a_1 + n_2 a_{12}).$$

Substituting $a = n_1^2 a_1 + 2 n_1 n_2 a_{12} + n_2^2 a_2$ for a , and the linear relation $b = n_1 b_1 + n_2 b_2$ for b in the case of *two* components, the expression for μ_1 becomes :

$$\begin{aligned} \mu_1 = & -k_1 T (\log T - 1) - RT (\log (V-b) - 1) + [(e_1)_0 - T(\eta_1)_0] + \\ & + \frac{\sum n_1 \cdot RT}{V-b} b_1 - \frac{2}{V} (n_1 a_1 + n_2 a_{12}) + RT \log n_1, \dots \dots \dots (1) \end{aligned}$$

in agreement with what I wrote down in my first communication.

If now we write $n_1 = 1-x$, $n_2 = x$, this then becomes :

$$\begin{aligned} \mu_1 = & -k_1 T (\log T - 1) - RT (\log (V-b) - 1) + [(e_1)_0 - T(\eta_1)_0] + \\ & + \frac{RT b_1}{V-b} - \frac{2}{V} [(1-x) a_1 + x a_{12}] + RT \log (1-x). \end{aligned}$$

For the determination of the complete function of x , which occurs here outside $RT \log (1-x)$, we will now determine the value of

$$\frac{RT b_1}{V-b} - \frac{2}{V} [(1-x) a_1 + x a_{12}].$$

The term with $\log (V-b)$ is supposed to be but very little dependent on x in regard to these two. If in the equation of condition we put $p = 0$, which is certainly permissible in the case of liquid phases,

then $\frac{RT}{V-b}$ may be replaced by $\frac{a}{V^2}$, and the above expression becomes :

$$\frac{((1-x)^2 a_1 + 2 x (1-x) a_{12} + x^2 a_2) b_1}{V^2} - \frac{2 ((1-x) a_1 + x a_{12})}{V}.$$

If now we replace V by b , which will hold for liquids at low temperatures in approximation, we obtain :

$$\frac{((1-x)^2 a_1 + 2x(1-x)a_{12} + x^2 a_2) b_1 - 2((1-x)a_1 + x a_{12})((1-x)b_1 + x b_2)}{b^2},$$

or:

$$\frac{-a_1((1-x)^2 b_1 + 2x(1-x)b_2) - 2a_{12}x^2 b_2 + a_2 x^2 b_1}{b^2},$$

which we may also write as

$$-\frac{a_1}{b_1} + \frac{a_1 b_2^2 - 2a_{12} b_1 b_2 + a_2 b_1^2}{b_1 b^2} x^2.$$

We therefore finally and approximately obtain:

$$\mu_1 = -k_1 T(\log T - 1) - RT(\log(V_1 - b_1) - 1) + [(e_1)_0 - T(\eta_1)_0] - \frac{a_1}{b_1} + \frac{A}{b_1} \frac{x^2}{b^2} + RT \log(1-x),$$

when we call

$$a_1 b_2^2 - 2a_{12} b_1 b_2 + a_2 b_1^2 = A.$$

The corresponding expression for μ_2 evidently becomes:

$$\mu_2 = -k_2 T(\log T - 1) - RT(\log(V_2 - b_2) - 1) + [(e_2)_0 - T(\eta_2)_0] - \frac{a_2}{b_2} + \frac{A}{b_2} \frac{(1-x)^2}{b^2} + RT \log x.$$

As (omitting p) it follows from the equation of condition, that

$$V - b = \frac{RTV^2}{a} = \frac{RTb^2}{a},$$

and that, therefore, $\log(V_1 - b_1) = \log \frac{Rb_1^2}{a_1} + \log T$, we may write in general:

$$\left. \begin{aligned} \mu_1 &= e_1 - c_1 T - (k_1 + R) T \log T + \alpha_1 \frac{x^2}{(1+rx)^2} + RT \log(1-x) \\ \mu_2 &= e_2 - c_2 T - (k_2 + R) T \log T + \alpha_2 \frac{(1-x)^2}{(1+rx)^2} + RT \log x \end{aligned} \right\} (2)$$

In this equation then

$$e_1 = (e_1)_0 - \frac{a_1}{b_1}; \quad e_2 = (e_2)_0 - \frac{a_2}{b_2}$$

$$c_1 = (\eta_1)_0 - (k_1 + R) + R \log \frac{Rb_1^2}{a_1}; \quad c_2 = (\eta_2)_0 - (k_2 + R) + R \log \frac{Rb_2^2}{a_2},$$

whilst

$$\frac{A}{b_1^3} = \alpha_1 \quad \text{and} \quad \frac{A}{b_2 b_1^2} = \alpha_2,$$

and also

$$\frac{-b_1 + b_2}{b_1} = r.$$

Remark. The quantity $\mu_1 = \frac{\partial \zeta}{\partial n_1}$ may also be obtained by the operation $\mu_1 = \zeta - x \frac{\partial \zeta}{\partial x}$. For the term $-\int p dV + pV$, occurring in ζ , may be written $-\int p dV = -RT \log(V-b) - \frac{a}{V}$. The required function of x may therefore also be found by calculating $(V=b,$

$$-\left(\frac{a}{b} - x \frac{\partial}{\partial x} \left(\frac{a}{b}\right)\right),$$

for which we then find exactly in the same way as above:

$$-\frac{a_1}{b_1} + \frac{a_1 b_2^2 + a_2 b_1^2 - 2a_{12} b_1 b_2}{b_1 b_2^2} x^2.$$

The two methods of calculation are, of course, identical. The last has the advantage, that we see at once that the differentialcoefficient of the correctionterm of x , i. e. $\frac{2Ax}{b^3}$, is nothing but $x \frac{\partial^2}{\partial x^2} \left(\frac{a}{b}\right)$, so that we have:

$$\frac{1}{x} \frac{\partial \mu'_1}{\partial x} = -\frac{1}{1-x} \frac{\partial \mu'_2}{\partial x} = -\frac{\partial^2 \zeta'_1}{\partial x^2} = \frac{\partial^2}{\partial x^2} \left(\frac{a}{b}\right) = \frac{2A}{b^3},$$

when ζ' , μ'_1 and μ'_2 represent the quantities ζ , μ_1 and μ_2 with omission of the terms containing $\log(1-x)$ and $\log x$. As regards the quantity

$\mu_1 = \frac{\partial \zeta}{\partial x}$, we must remember, that this is also obtained from the relation

$$\mu_2 = \zeta + (1-x) \frac{\partial \zeta}{\partial x}.$$

3. It is now the question, whether the expression

$$\alpha_1 \frac{x^2}{(1+rx)^2}$$

represents the melting-points of the tin-amalgams as well as, or better than my semi-empirical expression

$$\alpha_1 x^2 + \beta_1 x^3 + \gamma_1 x^4.$$

Let us first observe, that VAN DER WAALS always found α_1 *negative* in the case of electrolytes and other aqueous solutions (l. c. p. 195).

Now it is evident, that if we may write $a_{12} = \sqrt{a_1 a_2}$, the coefficient α_1 becomes $\frac{(b_2 \sqrt{a_1} - b_1 \sqrt{a_2})^2}{b_1^3}$, and ought therefore to be always found

positive. (I found for instance α_1 *positive* with tin-amalgams). It therefore seems, that when one of the components (water for instance) is an *associating* substance, or when the other component is *electrolytically dissociated*, we must certainly *not* follow D. BERTHELOT in writing $a_1 a_2 = a^2_{12}$, independent of the fact, that in such cases neither a_1 and a_2 , nor b_1 and b_2 are constants.

The formule (8) in my previous communication now becomes:

$$T = T_0 \frac{1 + \frac{1}{q_0} \frac{\alpha_1 x^2}{(1+rx)^2}}{1 - \frac{RT_0}{q_0} \log(1-x)},$$

or with $\frac{\alpha_1}{q_0} = \alpha$, $\frac{RT_0}{q_0} = \theta$:

$$T = T_0 \frac{1 + \frac{\alpha x^2}{(1+rx)^2}}{1 - \theta \log(1-x)} \cdot \cdot \cdot \cdot \cdot \cdot \quad (8bis)$$

From observations, where the values of x are less than 0,1, the value of θ was found to be exactly 0,396¹⁾. If we now further accept for the values of the coefficients α and r :

$$\alpha = 0,0453; \quad r = -0,74,$$

which are calculated from other observations with higher values of x , we obtain ($T_0 = 273,15 + 231,63 = 504,8$) the survey on the next page.

We notice, that in this table the agreement is an excellent one; the average deviation is about 0,9°, whilst in the case of the empirical formula with βx^2 and γx^3 (see previous communication), if the last value is not counted, it amounted to 0.85°. VAN DER WAALS'S expression for the correctionterm, therefore, represents at least equally well the course of the meltingpoint-line over the portion, observed from 212° to 65°. But what is still more important, is the fact, that whilst my former empirical formula does not very accurately represent the two last observations (the difference in the last even amounted to 10°), VAN DER WAALS'S expression not only satisfactorily represents these, but also the four observations at still lower temperatures (compare p. 22 of VAN HETTEREN'S Dissertation). In this observations the values of x and t were determined by analysis of the liquid phase, which is in equilibrium with the solid phase at a given temperature.

¹⁾ In the previous communication 0.400 was accepted, but $\frac{200}{505} = 0,396$ is somewhat more accurate.

x	x^2	Denom. $1 - \theta \log(1-x)$	αx^2	$(1+rx)^2$	Numerat. $1 + \frac{\alpha x^2}{(1+rx)^2}$	$T-273^{\circ}.15$	id.	Δ
						calculated	found	
0.1005	0.0101 ⁰	1.0420	0.00045 ⁸	0.8567	1.0005	211.6	211.6	0
0.1716	0.0294 ⁵	1.0745	0.03133 ¹	0.7621	1.0018	197.5	198.6	-1.1
0.2338	0.0546 ⁶	1.1054	0.00247 ⁶	0.6839	1.0036	185.2	183.7	+1.5
0.2969	0.0881 ⁵	1.1395	0.00399 ³	0.6089	1.0066	172.8	173.0	-0.2
0.3856	0.1487	1.1930	0.00673 ⁶	0.5108	1.0132	155.6	155.2	+0.4
0.5001	0.2501	1.2745	0.01133	0.3968	1.0286	134.3	133.4	+0.9
0.5973	0.3568	1.3602	0.01616	0.3114	1.0519	117.3	115.2	+2.1
0.6467	0.4182	1.4119	0.01894	0.2719	1.0697	109.3	107.4	+1.9
0.6754	0.4562	1.4456	0.02067	0.2502	1.0826	105.0	103.4	+1.6
0.6813	0.4642	1.4528	0.02103	0.2458	1.0856	104.0	102.4	+1.6
0.7104	0.5047	1.4907	0.02286	0.2250	1.1016	99.9	99.0	+0.9
0.7155	0.5119	1.4978	0.02319	0.2214	1.1048	99.2	98.8	+0.4
0.7477	0.5591	1.5454	0.02533	0.1995	1.1270	95.0	95.4	-0.4
0.7547	0.5696	1.5565	0.02580	0.1949	1.1324	94.1	94.0	+0.1
0.7963	0.6341	1.6301	0.02873	0.1687	1.1703	89.3	90.0	-0.7
0.8189	0.6706	1.6767	0.03038	0.1552	1.1957	86.8	88.4	-1.6
0.8921	0.7958	1.8817	0.03605	0.1155	1.3121	78.9	79.7	-0.8
0.9483	0.8993	2.1731	0.04074	0.0889 ⁸	1.4579	65.5	65.2	+0.3

x	x^2	Denom.	αx^2	$(1+rx)^2$	Numerat.	$T-273^{\circ}.15$	id.	Δ
						calculated	found	
0.9879	0.9759	2.7482	0.04421	0.0723 ¹	1.6114	22.9	25.0	-2.1
0.9903	0.9807	2.8357	0.04443	0.0714 ⁰	1.6223	15.7	15.0	+0.7
0.9941	0.9882	3.0326	0.04477	0.0699 ¹	1.6403	— 0.1	0.0	-0.1
0.9964	0.9928	3.2282	0.04497	0.0690 ¹	1.6516	— 14.9	-18.8	+3.9

The agreement is even unexpectedly great, when we consider, that the meltingpoint-line runs here almost vertical, and a quite insignificant change in x causes a difference of several degrees in T .

4. Let us examine the formula

$$T = T_0 \frac{1 + 0,0453 \left(\frac{x}{1 - 0,74 x} \right)^2}{1 - 0,396 \log(1 - x)}$$

more closely. With small values of x it passes into

$$T = T_0 \frac{1 + 0,0453 x^2}{1 + 0,396 (x + \frac{1}{2} x^2)} = T_0 [1 - 0,396 x + 0,004 x^2].$$

Because the coefficient of x^2 is *accidentally* nearly 0, the melting-point-line in this case runs over a fairly large region (from 232° to 120°) as an almost *straight line*. To ensure this, it is generally necessary, that $\theta^2 - \frac{1}{2} \theta + a$ is very small or 0.

As, for equilibrium between the solid tin and the tin in the amalgam, $\mu = \mu_1$ or

$$-\mu + \mu_1 = 0,$$

we also have:

$$\frac{\partial}{\partial T} (-\mu + \mu_1) + \frac{\partial}{\partial x} (-\mu + \mu_1) \frac{dx}{dT} = 0.$$

Now according to a well-known theorem $\frac{\partial}{\partial T} (-\mu + \mu_1) = -\frac{q}{T}$. The molecular potential μ for the solid phase is moreover not dependent on x . Therefore:

$$-\frac{q}{T} + \frac{\partial \mu_1}{\partial x} \frac{dx}{dT} = 0,$$

and consequently

$$\frac{dT}{dx} = \frac{T \partial \mu_1}{q \partial x}.$$

We therefore see, that supposing the solid phase (as in this case) contains no mercury, $\frac{dT}{dx}$ cannot become 0, unless $\frac{\partial \mu_1}{\partial x} = 0$. But then the liquid phase will be *unstable*, and we find ourselves on the spinodal line, so that the liquid amalgam would long ago have broken up into two phases of different composition.

Now, $\frac{\partial \mu_1}{\partial x}$ and therefore also $\frac{dT}{dx}$ may become zero in the case of *two* values for x ; there are therefore in this case always two horizontal tangents. A limiting case of this is of course a point of inflection with only one horizontal tangent.

As

$$\frac{d^2T}{dx^2} = \frac{T}{q} \frac{\partial^2 \mu_1}{\partial x^2} + \frac{\partial \mu_1}{\partial x} \frac{d}{dx} \left(\frac{T}{q} \right),$$

this limiting case will evidently occur when

$$\frac{\partial \mu_1}{\partial v} \quad \text{and} \quad \frac{\partial^2 \mu_1}{\partial x^2}$$

are 0 at the same time. Now

$$\frac{\partial \mu_1}{\partial x} = -\frac{RT}{1-x} + \frac{2A}{b_1^3} \frac{x}{(1+rx)^3}; \quad \frac{\partial^2 \mu_1}{\partial x^2} = -\frac{RT}{(1-x)^2} + \frac{2A}{b_1^3} \frac{1-2rx}{(1+rx)^4},$$

so that for this point of inflection we shall have the relations

$$\frac{x(1-x)}{(1+rx)^3} = \frac{RT}{2a_1} \quad ; \quad \frac{(1-x)^2(1-2rx)}{(1+rx)^4} = \frac{RT}{2a_1}.$$

On dividing, we find :

$$x(1+rx) = (1-x)(1-2rx),$$

or

$$rx^2 - 2(1+r)x + 1 = 0.$$

When r is either negative or positive, we find from this :

$$x_c = \frac{1+r-\sqrt{1+r+r^2}}{r}, \quad (a)$$

when x_c indicates the value of x at the point of inflection. x_c may run from $1/2$ (if $r=0$) to 1 (if $r=-1$), when r is *negative*. If, however, r is *positive*, x_c runs from $1/2$ (if $r=0$) to 0 (if $r=\infty$). The positive sign for $\sqrt{1+r+r^2}$ would give in both cases impossible values for x_c .

We now further obtain :

$$\frac{x_c(1-x_c)}{(1+rx_c)^3} = \frac{RT}{2aq_0} = \frac{RT_0}{q_0} \cdot \frac{1}{2a} \cdot \frac{T}{T_0} = \frac{\theta}{2a} \cdot \frac{T}{T_0},$$

that is to say, when for $\frac{T}{T_0}$ is substituted its value from (8bis) :

$$\frac{x_c(1-x_c)}{(1+rx_c)^3} \leq \frac{\theta}{2a} \cdot \frac{1 + \frac{a x_c^2}{(1+rx_c)^2}}{1 - \theta \log(1-x_c)},$$

where the lower sign indicates conditions, where $\frac{\partial \mu_1}{\partial v} < 0$, and which are consequently *stable*. From this then follows :

$$2a \frac{x_c(1-x_c)}{1+rx_c} (1 - \theta \log(1-x_c)) \leq \theta [(1+rx_c)^2 + a x_c^2].$$

Now, from the equation, from which (a) was deduced, we find :

$$1 + r x_c = 3 \frac{1-x_c}{2-x_c},$$

so that also

$$\frac{2}{3} \alpha x_c (2-x_c)^3 (1 - \theta \log(1-x_c)) \leq \theta [9(1-x_c)^2 + \alpha x_c^2 (2-x_c)^2],$$

consequently

$$\alpha \leq \frac{27\theta(1-x_c)^2}{x_c(2-x_c)^2[2(2-x_c)(1-\theta \log(1-x_c)) - 3\theta x_c]} \dots (b)$$

If, therefore, $\alpha =$ or $>$ than this value, then $\frac{\partial \mu_1}{\partial x}$ becomes 0 on one or two places on the meltingpoint-line.

From the expression for $\frac{\partial \mu_1}{\partial x}$ (see above) it follows immediately,

that when A , and consequently α , should be *negative*, $\frac{\partial \mu_1}{\partial x}$ can never become 0, still less positive. The occurrence of *unstable* conditions on the meltingpoint-line may, therefore, only be expected in the case of *positive* α , and only then, as soon as α reaches or exceeds the value, given by (b).

The relations (a) and (b), when united, give therefore the condition for *stable* phases along the *entire* meltingpoint-line.

In our example $r = -0.74$, and (a) gives $x_c = 0.863$. The equation (b) further gives with $\theta = 0.396$:

$$\alpha \leq \frac{27 \times 0,396 \times (0,137)^2}{0,863 \times (1,137)^2 [2 \times 1,137 (1 - 0,396 \log 0,137) - 3 \times 0,396 \times 0,863]},$$

that is to say

$$\alpha \leq \frac{0,180}{2,274 \times 1,787 - 1,025} \text{ or } \leq \frac{0,180}{3,04} \text{ or } \leq 0,0592.$$

Now, in our case α was 0,0453, so that everywhere we find ourselves in the stable region (as may in fact be seen from the shape of the observed meltingpoint-line). If α had been 0,059, we should have had a point of inflection with horizontal tangent; and had α been 0,059, we should have noticed the occurrence of a horizontal tangent in two places of the meltingpoint-line. This last case is, of course, not realisable, as the liquid amalgam would break up into two heterogenous liquid phases of different composition. ¹⁾

¹⁾ It is perhaps not devoid of importance to observe, that when the *solid* phase forms a *solid solution* of the two components, the presence in the meltingpoint-line of a point of inflection with a *horizontal* tangent points as before to *unstable* conditions. For in the general relation

Another question is, at what values of x and T does $\frac{\partial \mu_1}{\partial x}$ first become 0, or where does the plait commence, independent of the fact whether we find ourselves on the meltingpoint-line or not, which had just been investigated.

We have only to combine the relations $\frac{\partial \mu_1}{\partial v} = 0$ and $\frac{\partial^2 \mu_1}{\partial v^2} = 0$

$$\frac{dT}{dx} = T \frac{(x_2 - x_1) \frac{\partial^2 \zeta_1}{\partial v_1^2}}{v_{x_1}}$$

$\frac{dT}{dx}$ always becomes 0 in *one* place only in consequence of $x_2 - x_1$ becoming 0,

whilst on account of $\frac{\partial^2 \zeta_1}{\partial v^2}$ becoming 0, $\frac{dT}{dx}$ always becomes 0 in *two* places, or

in the limiting case in *two coinciding* places in a point of inflection with a horizontal tangent. DE VISSER thinks he has found such a point of inflection with mixtures of stearic and palmitic acids.¹⁾ It is, of course, not impossible, that we are dealing here accidentally with a case, in which the quantity x possesses the value indicated by (*b*). That the line of the end-solidifyingpoints also shows in the immediate neighbourhood a similar point of inflection, points to the fact, that the

conditions $\frac{\partial^2 \zeta}{\partial v^2} = 0$, $\frac{\partial^3 \zeta}{\partial v^3} = 0$ are fulfilled on both lines at about *the same time*,

which renders it more accidental still, because x would then possess the value required for this also in the *solid* phase. It should be pointed out, that as a rule

the conditions $\frac{\partial^2 \zeta}{\partial v^2} = 0$, $\frac{\partial^3 \zeta}{\partial v^3} = 0$ for *both* phases by no means include $x_1 = x_2$. For

this requires $\frac{\partial \zeta_1}{\partial v_1} = \frac{\partial \zeta_2}{\partial v_2}$. It is therefore a new accident, that both points of

inflection appear to coincide. But for this a reason may be given here. From the equation, from which (*a*) is found, namely $rx^2 - 2(1+r)x + 1 = 0$, it follows that with $r=0$, $x = 1/2$. DE VISSER now found both points of inflection to be at x about $1/2$ ($= 0.525$), so that the quantity r , both in the solid and liquid phase, is about 0 ($b_1 = b_2$). And in that case the values of x at both points of inflection *must* agree, namely both at $x = 1/2$.

The case, studied by DE VISSER, *may* therefore be an accidental coincidence of the two points of inflection. But then, on account of $\frac{\partial^2 \zeta_1}{\partial v_1^2} = 0$ and $\frac{\partial^2 \zeta_2}{\partial v_2^2} = 0$, both

the *liquid* and *solid* phases must have broken up into two layers, although of *identical* composition. The smallest delay in solidification would however immediately have carried the system within the plait, and then both phases would have broken up into two layers of a *somewhat differing* composition. It is however more probable, that both lines *nearly* show a point of inflection with a horizontal tangent, and that they *approach very near*, but *not touch* each other.

¹⁾ Rec. Trav. Chim. (2) T. 2, N^o. 2 and 4 (1898).

to find the values of x and T at the "critical" point. We find as above :

$$x_c = \frac{1+r-\sqrt{1+r+r^2}}{r} \dots \dots \dots (3a)$$

The temperature T_c of this critical point is found from $\frac{\partial \mu_1}{\partial x} = 0$, that is to say from

$$\frac{x_c(1-x_c)}{(1+rx_c)^3} = \frac{\theta}{2\alpha} \frac{T_c}{T_0}$$

We consequently find:

$$T_c = T_0 \frac{2\alpha}{\theta} \frac{x_c(1-x_c)}{(1+rx_c)^3},$$

or, as $1 + rx_c = 3 \frac{1-x_c}{2-x_c}$:

$$T_c = \frac{1}{27} T_0 \cdot \frac{2\alpha}{\theta} \frac{x_c(2-x_c)^3}{(1-x_c)^2} \dots \dots \dots (3b)$$

At this, or at lower temperatures, $\frac{\partial \mu_1}{\partial x}$ being then positive, we find ourselves therefore in the plait.

In the case of tin and mercury we find for x_c the value 0,863 (see above), if $r = -0,74$. For T_c we find:

$$T_c = \frac{504,8}{27} \times \frac{0,0906}{0,396} \times 67,60 = 289^{\circ}.2.$$

The "critical" point is therefore situated at 16° C., that is to say fully 57° lower than the point of the meltingpoint-line, belonging to $x = 0,863$ (13,7 atom-percent tin), namely $83^{\circ}.2$ C.

There are of course cases, where that distance is smaller, and where consequently a trifling supercooling already carries us within the region of the plait, which then — in the absence of the solid phase — causes a separation into two layers.

I may observe, that the value x_c does not correspond as a rule with a point of inflection (with oblique tangent) on the meltingpoint-line, when the critical point is not situated *on* the meltingpoint-line.

For $\frac{\partial \mu_1}{\partial x} = 0$, $\frac{\partial^2 \mu_1}{\partial x^2} = 0$ do not lead to $\frac{d^2 T}{dx^2} = 0$, when these differential-coefficients do not become 0 *on* the meltingpoint-line.

5. The value of q , the heat of fusions of tin in the liquid amalgam, is evidently:

$$q = q_0 \left(1 + \frac{\alpha x^2}{(1+rx)^2} \right).$$

When the value of x is small, and assuming, that mercury dissolved in tin is *monatomic*, we find for q_0 by calculation 2550 gram-cals. PERSON found experimentally 1690 gram-cals. Should this figure be confirmed, it would prove, that the associationfactor of mercury is about 1.5.

Now, it follows from the above formula, that at 25° , where x is about 1, q ought to be

$$= 2550 \times 1,6114 = 4110 \text{ gram-cals.},$$

whilst VAN HETEREN, by electromotive measurements, found about 3000 gram-cals. From this it would follow, that the value, used for q_0 , is about 1.4 times too large, which would be a confirmation of the fact, that the mercury in the amalgam is not present as single atoms.

In order to obtain certainty as regards the molecular condition of the *tin* in the amalgam, it would be necessary to know the melting-point-line of the *mercury*, and to determine the lowering of the melting-point in addition to the heat of fusion in the presence of very small quantities of tin. There are indeed indications, that the tin is also not present as single atoms. Indeed, the quantity $v = -b_1 + b_2$, which was found by us to be $-0,74$, gives for $\frac{b_2}{b_1}$ the value 0.26, from which it would follow, that the molecular volume of tin (b_1) would be about four times larger than that of mercury (b_2). Now, the atomic volume of Hg is 14,7, that of Sn = 16,1, so if these two components were monatomic, $\frac{b_2}{b_1}$ ought to be approximately = 1, whilst in reality that relation is $\frac{1}{4}$; this points to the probability, that in the case of tin several (may be six) atoms are united to one molecule.

It certainly would be highly desirable if this question were fully investigated. For in all our calculations the values of x are only then valid, when both mercury and tin are assumed to be monatomic. This is also the case with all similar calculations, relating to other amalgams.

May I be allowed to point out, that the molecular condition of *mercury* may be determined from the lowering of the melting-point of *tin*, if this contains *a little dissolved mercury* — whilst the molecular condition of tin may be ascertained from the lowering of the melting-point of *mercury* in the presence of a *little tin*. For in the case of *dilute* solutions something is learned only about the condition of the *dissolved substance*, but never anything as regards that of the solvent. In the limiting formula

$$T_0 - T = \frac{RTT_0}{q_0} x,$$

where T_0 and q_0 relate to tin as solvent for example, everything on the right hand side will remain unchanged, although tin should not be monatomic, but say n -atomic. For x , the concentration of the dissolved mercury, would then become n -times greater, but q_0 would also become n -times greater, because the heat of fusion relates to 1 mol. = n -atoms. On the other hand, if the mercury were m -atomic, the value of x alone would change; x would then become m -times smaller, and we shall, therefore, observe a m -times smaller lowering of the melting-point than that, calculated on the basis of mono-atomicity.

In this way we might attain to the knowledge of the molecular condition at the ends of the curve, x being 0 (for mercury), and 1 (for tin). But in order to form further conclusions with other values of x , the whole of the meltingpoint-line would have to be accurately examined, and this may in many cases become an exceedingly complicated matter.

6. There is, however, another way to get to know something about the molecular condition of the solid tin, and that is the composition of the *solid* phase, which is in equilibrium with the liquid one. If we equate the molecular potentials of *mercury* in the two phases, we obtain:

$$e_2 - c_2 T + RT \log x + \frac{\alpha_2(1-x)^2}{(1+rx)^2} = e'_2 - c'_2 T + RT \log x' + \frac{\alpha'_2(1-x')^2}{(1+r'x')^2}.$$

This further gives:

$$(e_2 - e'_2) - (c_2 - c'_2) T = RT \log \frac{x'}{x} + \left[\frac{\alpha'_2(1-x')^2}{(1+r'x')^2} - \frac{\alpha_2(1-x)^2}{(1+rx)^2} \right],$$

or with $e_2 - e'_2 = q'_0$, and with introduction of the meltingpoint T'_0 of pure mercury:

$$q'_0 \left(1 - \frac{T}{T'_0} \right) = RT \log \frac{x'}{x} + \text{id.},$$

therefore

$$q'_0 = \frac{RTT'_0}{T - T'_0} \left[\log \frac{x}{x'} + \left\{ \frac{\alpha_2(1-x)^2}{RT(1+rx)^2} - \frac{\alpha'_2(1-x')^2}{RT(1+r'x')^2} \right\} \right].$$

Now in the liquid condition

$$\alpha_2 = \alpha_1 \times \frac{b_1}{b_2} = \alpha q_0 \times \frac{b_1}{b_2}, \text{ so } \frac{\alpha_2}{RT} = \frac{\alpha q_0}{RT_0} \frac{T_0}{T} \times \frac{b_1}{b_2} = \frac{\alpha}{\theta} \times \frac{T_0}{T} \times \frac{b_1}{b_2}.$$

This quantity is therefore $0,1144 \times \frac{504,8}{298,2} \times \frac{50}{13} = 0,745$.

Putting $\alpha'_2 = \alpha_2$ and $r' = r$ as a first approximation, the value of the correction becomes:

$$0,745 \left\{ \left(\frac{0,012}{1 - 0,74 \times 0,988} \right)^2 - \left(\frac{0,99}{1 - 0,74 \times 0,01} \right)^2 \right\},$$

and, as at 25° the composition of the liquid phase was found $x = 0,988$, and that of the solid phase $x' = 0,01$ (perhaps 0,06), the said value becomes:

$$0,745 \times (0,0020 - 0,9950) = - 0,74.$$

A change of x' from 0,01 to 0,06 can only cause a slight alteration.

The value of the chief term $\log \frac{x}{x'}$ is:

$$\log^{10} \frac{0,988}{0,01} \times 2,3026 = 4,59,$$

so that we obtain (at 25°):

$$q'_0 = \frac{2 \times 298,2 \times 234,5}{63,7} \times 3,85 = 8450 \text{ gram-cals.},$$

whereas PERSON found $q' = 2,82 \times 200,3 = 565$ gr. cal. We therefore find a value 15 times too great. And a small error in the correction term 0,74 cannot upset this result. If, however, the tin in the solid amalgam is taken as hexatomic, x' becomes six times greater and q'_0 comes down to about 4400 gram-cals. If, moreover, x' is originally taken not as 0,01, but as 0,06, so that with a hexa-atomicity x' now becomes 0,32, the value q'_0 begins indeed to get more close to the value, obtained experimentally.

The above, therefore, contains indications enough of the polyatomicity of both mercury and tin. To arrive at a decision, however, accurate experiments will have to be made in the direction indicated, together with fresh determinations of the two heats of fusion.

Ethnology. — *“Influence of changed conditions of life on the physical and psychical development of the population of Central Borneo.”* By Dr. A. W. NIEUWENHUIS.

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

There is great diversity of opinion among competent authorities about the influence exerted by external circumstances of life on the development of a person and on that of the peculiarities of a tribe.

If this difference of opinion already gives evidence of the difficulty, of determining this influence for the individual, the difficulty is greatly

increased, as soon as we try to find, between two groups of men, characteristic differences, which are to be ascribed to their different circumstances of life. Examining the highly cultured nations which live in very complicated conditions of life, the difficulties become almost insuperable.

We are not a little hampered in this investigation by the fact that among civilized nations mutual intercourse and mixture have a disturbing influence on the eventual effect of special conditions of existence.

In Europe some data are furnished by the Israelites, which have preserved themselves as such for centuries in different countries under the circumstances prevailing there and which have absorbed few foreign elements. But here, too, the influencing conditions of life are very complicated, and the Israelites of the different countries have mixed with each other.

Chiefly because the relations in the societies of tribes, which have not reached so high a degree of civilization, are simpler and the conditions of life for all their members do not differ so much as elsewhere, it is likely that amongst them eventual changes in those conditions of life will stand out more prominently and that much becomes clear to the investigator, which was difficult to point out under more complicate relationships.

It is moreover noteworthy, that among them the influences of nature, of the surroundings in which they live, have a much greater effect than in higher civilized societies, which have learned to shield themselves better against this direct dependence.

We also meet with tribes where the great disturbing factor of frequent mutual intercourse and mixture is excluded in examining the modifications which two tribes have suffered by different external causes. A still simpler case presents itself where two large groups of the same race have lived for a long time under different external circumstances and have mixed little, if at all.

Before it has been proved that the people forming these tribes, are in their original qualities the same as Europeans, we must not directly apply what has been observed in them, to European society. For the right understanding of the pre-historic course of the development of mankind, however, we may refer to the tribes, which have reached as yet but a lower degree of culture; in my opinion we are equally justified in drawing certain conclusions as to the corresponding influences on higher cultured nations from many things, which we have observed in the social matters of the former.

During my second journey through Borneo I had the privilege of

living among two groups of the same tribe, which have existed for a century and longer under very different circumstances. They were the Bahaus on the Upper-Mahakam, with whom I lived for two years, and the Kenjas on the Upper-Kajan, with whom I spent some months.

The tribe-groups of this name occupy together the upper- and middle course of all the rivers, which fall into the sea on the North coast, beginning with the river Batang-Rèdjang, and as far as the East coast, including the river Mahakam. They are called collectively the Pari-tribes, and they all consider the region containing the sources of the river Kajan as their original country. Mutual quarrels, the result of too dense a population, were the cause, that for centuries again and again tribes moved away to neighbouring rivers, as e.g. it happened no more than 25 years ago with the tribe Oema Timé, which settled on the Tawang, a tributary on the left of the Mahakam.

The Bahau-tribes on the Upper-Mahakam also originate from this native country, which they call Apo Kajan, but they have lived in their new home already for more than a hundred years. This was curiously confirmed on my arrival in Apo Kajan with my Bahau-escort. Their chieftain Kwing Irang then received for the first time a full account of the history of his ancestors, which was already forgotten in his own tribe.

How little intercourse the inhabitants of the Upper-Mahakam have with those of the Upper-Kajan may be derived from the fact that among all the younger Bahaus only one man had ever been in Apo Kajan, and that, when in the company of 60 Bahaus and 20 pseudo-Malays I set out on the expedition thither in August 1900 none of us knew the way. The journey lasted a month, and we had to traverse uninhabited land. The way was indicated by sticks put up in a special way in the river-mouths by some Kenjas who travelled in boats in front of us, the sticks denoting which rivers we had to take.

We may therefore assume as certain that we have to deal with tribes of the same origin, to which moreover their language, dress, morals and customs point, which distinguish them clearly from other tribes, e. g. from those on the Barito- and Lower-Batang Rèdjang. Their descending from Apo Kajan to the Upper-Mahakam, however, brought the Bahaus in peculiar conditions, which exercised a great influence on them. On the Upper-Mahakam, namely, the Bahaus live at a height of from 250 to 200 metres, the Apo Kajan is 600 metres and higher. That this difference as regards the climate is very considerable especially in Borneo, may be derived from the

fact that in Java the region of moss vegetation does not begin lower than at a height of 2500 metres, whereas in Borneo it begins at a height of a thousand metres. This is caused by the following circumstances.

The situation of Borneo being under the equator, the middle region is but slightly affected by the influence of the trade-winds, which e. g. in Java make the difference between the wet- and the dry-monsoon so great. Hence it may happen that more rain falls from December to March than from May to October, but particularly in the highlands really dry times are unknown, and we may find low water in the rivers in the rainy period. The regular distribution of moisture through the whole year is greatly furthered by the circumstance that the whole island is covered with one large primitive forest, which itself retains large quantities of water, and harbours mouldering rocks which do the same. The annual rainfall amounting from 3000 to 5000 m.m. at different places, the climate is very humid all through the year, and the sky is always more or less overcast, so that a cloudless sky is a great rarity in the higher regions. Soon after sunset a low hanging curtain of clouds is formed in the valleys. This does not rise until seven o'clock in the morning or later and envelops the summits of the mountains till pretty late in the evening. In consequence of this the maximum temperature at a height of 250 metres is 30° C. in the shade on the Upper-Mahakam; at six o'clock in the morning however it was never lower than 20° C. Noteworthy is also that strong winds of long duration do not occur there, only some blasts of short duration, which are generally preceded by heavy showers.

The climate of Apo Kajan and of the Mahakam differs but little in most of its peculiarities, such as humidity, and a cloudy sky, but the latter is a good deal colder on account of the greater height, and what is particularly striking is the continually prevailing wind. This accounts for the fact that though in two months I never found a lower temperature than 17° C. at six o'clock a. m. and though it hailed but once, the climate is yet much rougher. The red cheeks, specially of the women and children prove this, and also the fact, that the different kinds of rice require a month longer to ripen in Apo Kajan than on the Mahakam. Yet the method of growing rice is the same, and consists in cutting down and drying the wood, after which it is burned and the rice sowed in holes, which are made by pushing pointed sticks into the soil, which is covered with ashes.

The geological formation is the same in Apo Kajan as on the Upper-Mahakam; we find in both a strongly denuded upland, where

everywhere old slate layers come to the surface. Only here and there younger formations, specially free-stone, cover the older.

If we now take into consideration that only in the last 30 years either the Bahaus on the Upper-Mahakam or the Kénjas on the Upper-Kajan have come into such close contact with higher civilized nations that it induced some of their men to undertake commercial enterprises for the purchasing of salt and linen, I think that I am justified in asserting that the two groups of tribes under consideration belong to the same race, that they have lived for upwards of a hundred years in countries with a different climate, that they have had but little mutual intercourse and have not mixed; that they have not changed their life as cultivators of the soil and have developed without external influences.

What effect this difference of climate can have on the population, may be derived from the fact, that in my opinion the thinness of the population in Borneo depends in the first place on the influences of the climate, and much more on the customs of the people than on the infectious diseases, such as cholera, smallpox, which are introduced from the coast. As both Upper-Kajan and Upper-Mahakam are so difficult to reach that infectious diseases but very seldom extend to them, we have, when trying to determine what the result of those changed conditions of life is for the Bahaus, only to deal with those factors which are sometimes comprised under the name of influences of the climate.

What is understood by influences of the climate in the highlands of Borneo became clear to me for the first time in the sultanate of Sambas on the West coast of the island, where I was struck by the difference in the spread of malaria among the population of the marshy coast regions and that of the highlands. In order to get a fuller knowledge of this difference, I made an inquiry into the traces of malaria infection on about 3000 children, both in the marshy alluvial plain and in the highlands. These children had not been offered to me on purpose for this investigation, but for an inquiry into the results of the vaccination among the Malay and Dajak population.

Among the population of the alluvial plains I found among 2103 children only 6 with a chronic hard splenic tumor, or 2,8 per 1000.

Among 420 children of the uplands it occurred in 403 children, or 959.5 per 1000.

The remaining 396 children originated from regions, which in their formation were the transition between the alluvial plains and the uplands. *Janus, Deuxième Année 1898.*

This inquiry yielded the result, that in the marshy alluvial plains which consist entirely of vegetable and animal remains, malaria hardly ever occurs, as opposed to the uplands where nearly all children suffer from chronic malaria-infection. At the same time I saw, that soon after birth the hardened and enlarged milt makes its appearance, for it was long before I could find a Dajak child of three weeks old, whose milt was not to be felt.

It is impossible to give the morbidity and the mortality caused by the malaria-infection among the population of the uplands in figures. I only found the death-rate in Sambas extending over 6 normal years, i. e. years without cholera or smallpox, to be for Dajaks 37 per 1000, for Malays 28 per 1000, which however does not represent the influence of the malaria, because there are also some Malays who live in the uplands and among those, who have chiefly settled in the lower plains, diseases of the digestive organs are much more frequent than among the hills.

In order to appreciate fully the influence of the malaria-infection on the existence of the inhabitants of the higher regions, we must dwell for a moment on the phenomenon, which prof. Koch says that he observed in New-Guinea, namely, that the native, who went through the malaria-process independently i. e. without any aid except his constitution, became immune against it. Many are the refutations adduced against this statement by physicians, who practised in New-Guinea. They all pointed out how frequently also adult Papoeas suffered from malaria.

Judging by my experiences among the Dajaks, the truth lies between the two. I also have been struck by the fact that not so many hard enlarged milts as symptoms of the malaria-infection are met with among adult Dajaks as among children under the age of ten, which certainly points to a less strong influence of this infection. Moreover there is a great difference between the action of chinine on Dajaks and on Europeans, who are not immune. Though we must make allowances for other factors than immunity, yet it is remarkable, that we obtained much greater results with at most 1 gram sulphas chinini a day among the Dajaks than with 2 to 3 gr. murias chinini among European soldiers, seized by malaria in Lombok.

Among the former it was possible to cure not only the acute cases of malaria, but also cases which had continued from 4 to 6 months and had not been treated before, by administering 1 gram sulphas chinini per day and per dose during 8 days, whereas in the first four months after the war in Lombok in a mixed garrison of 1500 men more than 500 Europeans had to be removed, most of them by far

being malaria patients, whom I myself had treated with from 2 to 3 grams per day and per dose, and who had little chance of being cured in Lombok itself.

Among at the least 2000 Dajak malaria patients, whom I treated specially in Central-Borneo and of whom hardly any died, I observed another telling difference between the reaction of their body against the malaria-infection and that of the Europeans.

Whereas under unfavourable circumstances many of the latter perished under rabid and strong symptoms, sometimes so quickly, that chinine was of no avail, such acute cases with strong icterus, unconsciousness and collapse were never found among the Dajaks. I saw, however, many cases where the disease had reached an advanced stage after protracted illness.

That this difference was not due to the inferior strength of the infection in Borneo, was proved by my European and native fellow-travellers, most of whom suffered badly from malaria; to them I had again to administer from 2 to 3 grams of murias chinini a day, and one of them I had to give a strong hypodermic injection of 3,25 gram chinine within 36 hours.

From all this we may assume that the Dajaks become partially immune if in youth they are subjected to repeated attacks of malaria. Yet even then whatever weakens the constitution may give rise to attacks of malaria, so that diseases of the respiratory organs or of the digestive organs, wounds, diseases of infection and specially everything that is comprised under the name of catching cold, get complicated with malaria.

As the mountainous regions on the Upper-Mahakam are among those where malaria is of very frequent occurrence, it is clear, that the Bahau-population suffer greatly from it and that the individual experiences its enfeebling influence from early youth till death.

Being used for years in my practice among them to find that the great majority of cases were those of malaria, I was greatly struck by the change after my arrival among the Kënja population of Apo Kajan. I must add that my reputation as a physician procured me immediately after my arrival a great number of patients, though only few had ever seen a European on the coast before.

It first struck me, that so many hydropic old people called in my help, which had scarcely ever occurred in lower regions; whereas the malaria-cases retired to the background and during my stay confined themselves to a few acute cases. I found then, that the change in the sick-rate of the population was chiefly due to the prevalence of bronchitis with emphysema and heart-disease, bronchitis

being caused by the rough climate and increased by the smoking of badly prepared tobacco, which even very young children begin and which is held to be a remedy against coughing.

Though more acute malaria cases occurred, when the rough, cold weather set in with violent showers, there was not any question of a chronic infection of the population, manifesting itself in an enlarged, hardened milt in the children. This agrees with the well-known fact, that in a rougher colder climate malaria generally decreases in violence.

As bronchitis and its consequences do not make their enfeebling influence felt on the constitution before a more mature age is reached and are not to be compared in this respect with strong malaria-infection, I believe to have found the chief factor of the present difference of the two groups of the same tribe as to their constitution and their character in the difference of the occurrence of malaria as a consequence of the difference in height of the country of the Bahaus and that of the Kénjas.

Moreover I must take into account that syphilis is found in a less violent degree among the Kénjas than among the Bahaus. Among some Bahau tribes it was so universal, that I thought the fact that only tertiary forms were found could be explained by assuming exclusively hereditary transmission. Among the Kénjas, however, syphilis was also met with only in that form, but the cases were so isolated that we could not possibly ascribe them to hereditary influences. The cases observed seemed to have a less injurious influence on the general condition of the Kénjas than on that of the Bahaus. That this endemic form of syphilis is so much less common and that its symptoms are so much less dangerous among the Kénjas than among the Bahaus is due to a great extent to their stronger constitution.

If we now take into consideration, that among all these tribes every family, even that of the chiefs is dependent for its daily food and sustenance on the continual labour of all its members, which is not the case in more highly civilized societies, we feel, how great the influence must be which the more or less frequent occurrence of these diseases must have on the prosperity of the tribe.

A striking example of the better conditions of existence offered by Apo Kajan which is of equal extent to the Upper-Mahakam, compared with the lower river-basins, is furnished by the fact that for centuries many tribes have been leaving this country for other parts of the world and that nevertheless the population there is at present much denser than in other Dajak regions:

Instead of 300 to 800 inhabitants as on the Upper-Mahakam, the villages count there 1500—2500 inhabitants, though they certainly do not lie farther apart. Moreover the general appearance of the Kénjas makes a much better impression because of their stronger build and the less frequent occurrence of deforming diseases among the scantily dressed figures, which is enhanced by the absence of the cachectic persons so numerous elsewhere.

The difference between the Bahaus and the Kénjas is even more marked in their psychical qualities than in their physical individuality. The enfeebling moments, which on the Mahakam affect them in a so much larger degree seem to have had a strong degenerating effect on the psyche of the Bahaus.

This is proved by their history: in the beginning of the 19th century they made themselves known not only by head hunting but also by raids undertaken on a larger scale till far into the river-basin of the Kapoewas, the Barito and the Mahakam, in which regions no tribe could resist them; at present smaller forays rarely occur, larger expeditions are quite out of the question and in a fight with other tribes the wounding or death of one man may put his tribe to flight.

The greatest difficulties which confronted the European stranger in his intercourse with the Bahaus, arose in his continual struggle with their timidity, fear and suspicion even after a long intercourse and in the fact that his movements were continually hampered by the peculiar religious and other convictions of these tribes. The strong contrast in these respects between them and the Kénjas is therefore very striking.

After my arrival in Apo Kajan I was at once struck by the fact, that the 150 men, who had come under their principal chieftain to assist me by bringing boats and improving roads, were much freer and noisier in their behaviour than my Bahau escort, that the chieftains gave their commands with much greater energy and that they were also better obeyed. During my stay in their villages this impression was greatly strengthened by the want of shyness on the part of the women and children. Remarkable was the contrast between the behaviour of the young Kénjas and the Bahaus when I, as I usually did, distributed small presents, such as beads, finger-rings, needles and pieces of cloth among them. Among the Bahaus I could quietly keep in my chair, and though occasionally a little hand may have been stretched out too quickly towards the coveted object, yet all the little ones waited patiently for their turn and never became boisterous. When I distributed things among the Bahaus, the proceedings were quite different: I had to begin with taking a

firm footing, for boys and girls pressed in upon me with loud shouts and extended hands; every one was afraid to be behind hand and they scuffled among each other, to get nearer. It soon proved that they are less sensible to the bad smells of their fellow-men than the Bahaus among whom one can sit for hours with impunity even in large companies; therefore they also prefer to go a long way round rather than pass a dead body, and who protest to a disagreeable smell by violent gestures and spitting.

Remarkable also is the greater perseverance of the Kénjas at labour, which I specially observed when making long expeditions in rowing-boats on the Mahakam in the great heat to which they were not used. Though they are more used to walking than to rowing in their highlands, where the roads are better and the rivers smaller than in the country of the Bahaus, yet they kept on rowing for days together much more persistently than the latter, and always arrived earlier.

These few examples already give evidence of a greater vivacity, less sensibility and also of a greater power of resistance of the nervous system; moreover their mental capacities are far superior.

When telling the Bahaus about some remarkable features of our society, I got accustomed to meet with an absolute incapacity to imagine these things, which gave rise to disbelief, and induced them, but often after a long interval, to try and catch me at an untruth. Among the Kénjas, however, I soon concluded from their questions, that they at least tried to imagine railroads and similar inventions, and that they really understood other things. A very good criterion is furnished by the explanation of the motion of the sun, the earth and the stars with the origin of night and day, and the causes of a solar- and lunar eclipse. Of course the Kénjas also did not immediately believe that the earth is round and moves, nor that it is not a monster that eats sun and moon in case of an eclipse, but they understood at least my explanation.

Of practical use to us was the greater interest and the more extensive knowledge of their surroundings shown by the Kénjas.

In the course of our topographical survey of the Mahakam and when inquiring into the names of the principal mountains and rivers we met among the Bahaus with such utter ignorance, that we were for a long time convinced they were unwilling to tell them to us. It proved however later on, that it was not unwillingness on their part, but that only few among them knew anything about rivers and mountains outside their immediate neighbourhood, and that e. g. high mountains, which, though they stood at some distance on the territory

of another tribe, but commanded the landscape, had no name among them, and that in order to find out its name, we had to apply to tribes living nearer the mountain. It was, of course, quite out of the question to avail ourselves of their help in determining the different places from such a mountain top.

I was therefore greatly struck, when among the Kénjas I ascended a mountain, for the purpose of getting a survey of their country and Boei Djalong, the chief of the country, who accompanied me pointed out all the mountains as far as the horizon with their names, also those we could verify in the Mahakam territory; he also indicated the roads leading to the different adjoining countries as accurately as a European could have done.

Not only we, but also the Bahaus who accompanied me, were astonished at the knowledge of the history of times long past, which the Kénjas displayed. It is a wellknown fact that tribes, who cannot write and who possess a low degree of civilization, lose quickly the memory of past events, and the knowledge of the Bahaus about their ancestors was therefore very inaccurate. Great was therefore the astonishment of Kwing Irang, when the Kénjas told him the traditions of his own ancestors during the time of their stay in Apo Kajan.

This greater development of their psyche keeps pace with phenomena, which evidence a stronger personality as regards their surroundings. They are braver, which appears clearly from their way of conducting warfare. The tribes in Borneo are notorious on account of their headhunting, a method of taking revenge and of fighting, which is justly looked upon as being rather cunning and cowardly than brave, as it consists in the laying of ambushes and the sudden attack of superior forces on but a few individuals. An open fight is rare among the Bahaus, and as has been said before, if two tribes are confronted, the death or wounding of one man suffices to put his party to flight. Quite different is the warfare among the Kénjas: hand-to-hand fights are frequent, in which chiefly the sword is used, and in which many are killed before the battle is decided. Though headhunting occurs also among them, yet it recedes more into the background, and when it occurs more personal valour is displayed. A few years ago e. g. a young Kénja chieftain, when performing a war-dance during a visit on the Mahakam, suddenly cut off the head of one of the spectators, and took it with him in his flight. This was certainly treacherous, but it requires courage to do such a thing in a large gallery with a great many lookers-on.

It is irritating to see, how the Bahaus submit to be illtreated by the Malays, who live at their expense by deceit, theft and grave-

robbery etc. Only rarely do they take revenge on these unwelcome guests, who live among them either because they gather the forest products, or because they had to fly from the coasts on account of crimes.

The Kënja-tribes are less long-suffering: two gangs of Malays, one consisting of five members from the Mahakam and one of eight from Sërawak, who tried to live upon them in a similar way, were all murdered.

As soon as we come in contact with the Kënjas, this bold personality impresses us favourably. Among the Bahaus we could not establish for years the frankness of intercourse between them and ourselves, which was brought about with the Kënjas in as many months. Only incidentally and by indirect means could I get to know among the Bahaus what they thought of a plan and what they intended to do. When alone with one of them I occasionally succeeded in getting him to express his thoughts freely, because he had no reason to be afraid of his fellow tribes-men, but they never quite relinquished their fear and distrust.

In our intercourse with the Kënjas the last trace of suspicion had soon vanished, and never shall I forget the impression made by their political meetings on us Europeans, used to the uncertain, hesitating and insincere behaviour of the Bahaus, even when discussing affairs of great importance. In the meeting of the Kënjas all the chiefs present freely expressed their opinions with peculiar ceremonies on subjects as e. g. whether it was advisable to adhere to the rajah of Sërawak or to the Dutch-Indian government, and the advantages and disadvantages were openly discussed.

If on account of these peculiar qualities the behaviour of the Kënjas is noisier, coarser, braver and less sensitive than that of the Bahaus, it is interesting to see what influence this has had on their society. Among the Bahaus on the Mahakam we find a number of perfectly unconnected tribes, in which every individual considers himself quite independent of all the others, and perfectly free to look upon his own interest as of chief importance, which renders the chiefs powerless to exert any influence over their subjects for more general interests and enterprises. Everybody entertains the greatest fear for unexpected sudden attacks from far or near, and while in the day-time the men always go to their rice-fields strongly armed, in the evening they dare not even be under their houses without a naked sword. Of course women and children are still more afraid.

Among the Kënjas, on the contrary, we find a somewhat loosely constructed, but yet connected whole of all the tribes under the

acknowledged supremacy of the tribe of the Oemo Tow and its chief Boei Djalong. The country is so safe, that the population goes to the fields only armed with a light spear as support, and that women unarmed and unaccompanied dared to come and visit me from neighbouring settlements at many hours' distance through the primitive forest or in boats.

In this better regulated society the higher moral qualities of the Kënjas also stood out to advantage. If among the Bahaus the want of interest in the public welfare was strongly felt, among the Kënjas this was different. In the character of the Kënja chiefs a sense of responsibility and disinterestedness came to the front accompanied with more moral courage and influence on their subjects. When questions arose as to wages, the payment of which always consisted in goods chosen by the party concerned, the Bahau chiefs always retired for fear of quarrels with their people. Among the Kënjas the chiefs calculated, how much was due to each of their people, took it home and distributed it there.

When it had been resolved in the political meetings, that representatives of several tribes should go with me to the Mahakam, hundreds of Kënjas prepared to go. Bad omens for the journey, however, caused more than 400 to draw back, and though the principal chiefs might have done so too, they only sent back their followers and went on themselves, because they felt the great importance of carrying on the negotiations.

Among the Bahaus no chief would easily have gone to look after the general interests, and certainly not against bad omens.

Also the conduct of their inferiors during the journey was quite different. Eighty Kënjas succeeded in deriving the required favourable omens from the flight of birds, the cries of does and the appearance of certain snakes, and accompanied us. Though from different villages, they formed one company, having their victuals in common, and when the Bahaus and ourselves had not enough they shared their stock with us, which was then soon exhausted. They had, however, full confidence in my assurance that I would buy them fresh provisions on the Mahakam.

The different groups in a Bahau escort never voluntarily share their rice with each other, and when I and my Malays were in want of rice on the journey, we could only get some from them at very high prices. At last a young man had the assurance to ask me three times that exorbitant price for his rice, though as a physician I had saved his life, and had treated all of them without asking any reward.

In spite of the great advantages, which the Bahaus derived from our stay, I never met with any direct proofs of gratitude; they only put somewhat greater confidence in me than in other strangers. When however I left a Kënja tribe after a six days' stay, the family of the chief came personally to thank me for everything I had given to them either by way of exchange, presents or medicine; the first expression of gratitude for many years.

All this proves that the Kënjas of Apo Kajan are far superior to the Bahaus also as regards those traits of character, which are considered as higher ones among Europeans.

Another striking example of their stronger personality is furnished by the way, in which their religious ideas influence their existence.

From their standpoint as agricultural tribes of fairly low development, with whom the influence of nature on their principal means of subsistence, agriculture, and on their persons in diseases and disasters is strongly felt, these peoples contemplate their surroundings with great fear. Their thoughts about these surroundings and the place they occupy in them, which represent their religious conviction, are not of a very elevated nature.

They think that their lives are ruled by one chief god, whom they call Tamei Tingei, our high father, and who punishes already on earth all crimes with adversity, disaster, disease and death. For the execution of his will he makes use of a host of evil spirits, who people all nature around.

All calamities and diseases, therefore, even death on the battlefield or at a confinement, are to these tribes the manifestations of anger of their chief god with regard to the sufferer, who has incurred this anger by the conscious or unconscious violation of human usages or divine laws.

When the attempts, to guard themselves against the manifestations of the anger of their god by observing these laws and usages scrupulously, proved fruitless, they tried to reach their aim by extending the prescribed laws to the minutest details, so that they have definite precepts as to the course to be followed not only in all emergencies of every day life, but also in agriculture, the chase and fishery.

All these precepts are called pëmali, and they render certain actions in certain cases lali, pantang or taboe.

If the observation of the pëmali is to shield them from the evil spirits, they enjoy the assistance of a whole multitude of good spirits, indirectly through the mediation of the priests and priestesses or directly by warning omens, which are communicated by certain birds, snakes and does, and also by certain events. These omens are very numerous, and are strictly followed, especially by the Bahaus.

As however these pëmali and omens have risen, independent of the true requirements of the existence of these tribes, they have constantly a disturbing influence. To give an example: the Bahaus, when growing rice, do not regulate their work according to dry or wet weather, or to the condition of their fields, but all the families of a tribe have to conform to what the chieftain does, and he sees that the necessary religious rites before the special successive agricultural proceedings are duly performed. When the preliminary rites for the sowing have commenced, no one is any longer allowed to burn dead wood on his field; if the chief is weeding, every one must cease his sowing, etc.

In the same way they begin all important enterprises, such as travelling, the building of a house, etc. not according to the demands of the moment, but according to whether a bird flies up to the right or to the left, and whether a doe is heard or not.

Of course, stronger races do not so meekly submit to the galling restraints of these pëmali and omens, as more timid natures. I had an opportunity of observing this as a characteristic difference between Bahaus and Kënjas. It is true that both have the same religion and that their pëmali and omens are essentially the same, but the pëmali are more developed among the Bahaus and go more into details, than among the Kënjas. Among the former all the adults in a tribe are obliged to observe the pëmali closely; among the Kënjas the priests are specially charged with this, so that the mass of the people have more liberty.

Among the Bahaus e.g. nobody eats the flesh of the stag; among the Kënjas the priests only do not take it.

The Kënjas have not introduced the above-mentioned very injurious precepts for the growth of rice with the same restrictions. It is true that also among them the chief causes the necessary ceremonies to be performed, but still, every one is free afterwards to do in his field, what will prove necessary, and this is of the greatest importance for the success of the harvest.

The Bahaus cling much more scrupulously to the existing pëmali and omens than the Kënjas. In spite of my having lived for years among the Bahaus, I was forced, to observe their precepts as scrupulously as they themselves did. Only in case of urgent necessity I dared set out on a journey or receive a patient during the time prohibited by their laws, and I was therefore as much shut out from the outer world as they were. Once they made the inhabitants of their own village on their return from an eight months' expedition remain in the forest, starving, rather than violate the lali of their village by admitting them or bringing them provisions,

When I arrived with my companions among the Kēnjas, the principal chief and his family happened to be in the condition of lali, but in order to be able to receive us he quickly had a new house built in another place for the priest family in his house, who were the principal bearers of the pēmali. By this means it was permissible for him to receive us in his house.

Later on we proceeded to another village, where the house of the principal chieftain was also lali. For our reception he divided his house, which was very long, into two parts by means of a gate, so that we strangers could not enter the one part. In the other he received us.

The Kēnjas watch the omens before every enterprise as earnestly as the Bahaus, but as soon as they are in conflict with the requirements of the moment, they dare take their own course to a much greater extent.

I have already mentioned that the Kēnja chiefs ventured to accompany me to the Mahakam in spite of the bad omens of their birds.

In case of imminent danger, e. g. if an enemy is thought to be hidden in the neighbourhood, the Kēnjas disregard omens.

So we see among the Bahaus the more scrupulous observance of a more developed system of religious usages keep pace with the deterioration of many of their physical and psychical qualities. In these the Bahau is inferior to the Kēnja, which can originally not have been the case, but which is owing to the change of abode of the Bahaus more than a hundred years ago, because through this change they were exposed to the more injurious influences of their new surroundings, the principal of which is a greater prevalence of malaria.

Mathematics. — Prof. P. H. SCHOUTE discusses: “*Relations between diagonals of parallelotopes*” with a view to show by a simple example how it is possible that investigations of more-dimensional figures lead to new theorems on figures of our three-dimensional space. This example relates, as the title indicates, to those figures which continue in the spaces with more than three dimensions the well-known series of line-segment, parallelogram, parallelepipedon . . . and can therefore be called by the name of parallelotopes. Here diagonal always denotes a line connecting — across the inner part of the enclosed space — two opposite vertices. *First* our attention may be drawn to the fact that the number of diagonals of the parallelotope is doubled

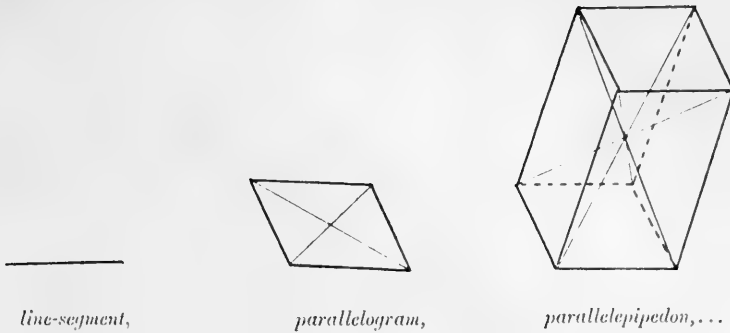


Fig. 1.

every time a new dimension is added, whilst the number of constants determining the figure, though at first larger than the number of diagonals, increases less strongly than the latter; this is illustrated by the following little table, where under each other the corresponding values of the number n of the dimensions, the number d of the diagonals and the number g of the determining constants are indicated, whilst the meaning of h is explained further on.

n	2	3	4	5	6	7	8	9	10	...	n
d	2	4	8	16	32	64	128	256	512	...	2^{n-1}
g	3	6	10	15	21	28	36	45	55	...	$\frac{1}{2} n(n+1)$
h			1	5	16	42	99	219	466	...	$2^{n-1} - \frac{1}{2} n(n-1) - 1$

From this is evident in the *second place* that when constructing parallelogram and parallelepipedon all diagonals can be used as determining lines, but that this is not possible for the parallelotope P_5 with five and for the following parallelotopes $P_6, P_7 \dots$ with still more dimensions; and from this ensues in the *third place*, what becomes the principal thing here, that between the 16 diagonals of P_5 at least *one* relation must exist and that this number of relations for $P_6, P_7 \dots$ must increase consecutively to 32—21 or 11, 64—28 or 36, ... If in the *fourth place* we wish to trace those relations and try to do so under the condition that the length of all the edges must figure amongst the determining data, then we find that the sum of the squares of all the diagonals — always equal to the sum of the squares of all the edges — is known at the same time, and that the other relations, between the diagonals only, always present themselves in the form of homogeneous equations, the number h of which is indicated above. This includes that already for the parallelotope P_4 we come across a relation between the diagonals. This simple relation can be expressed as follows: If we divide (Fig. 2) the eight vertices of one of the eight parallelepipeda forming the boundary of

the four-dimensional figure into two groups (A_1, A_2, A_3, A_4) and (B_1, B_2, B_3, B_4) of non-adjacent vertices, the sum of the squares of the diagonals terminating in the four points A is equal to the sum of the squares of the four remaining ones, terminating in the points B . And from this ensues, the common centre of the eight diagonals being indicated by O , the equation

$$OA_1^2 + OA_2^2 + OA_3^2 + OA_4^2 = OB_1^2 + OB_2^2 + OB_3^2 + OB_4^2,$$

or in words: If we divide the eight angular points of a parallelepipedon into two groups of four non-adjacent points, the sum of the squares of the distances from an arbitrary point O to the points of each of

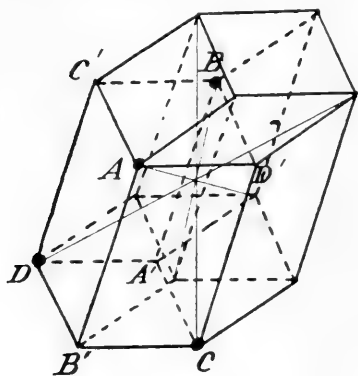


Fig. 2.

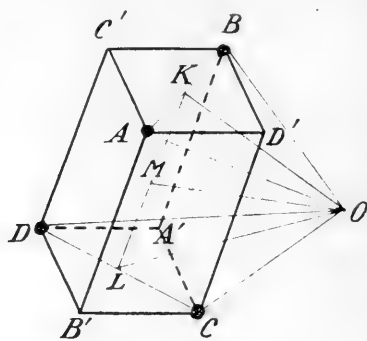


Fig. 3.

the two quadruples is the same. If we now suppose in the *jif*th place that this point O lies with the parallelepipedon in the same three-dimensional space, our space I may say, we finally find the following theorem belonging to our solid geometry:

“If we connect (Fig. 3) an arbitrary point O of space with the two quadruples of non-adjacent vertices of a parallelepipedon, we obtain two quadruples of line-segments for which the sum of the squares has the same value.”

This simple theorem which up till now I never came across in any handbook is of course easily proved; we have but to know the formula for the median line in a triangle. With the help of this formula we find that, disregarding quantities not depending on the place of O , the sum of OA_1^2 and OA_2^2 can be replaced by two times $OC_{1,2}^2$, the sum of OA_3^2 and OA_4^2 by two times $OC_{3,4}^2$ and twice the sum of $OC_{1,2}^2$ and $OC_{3,4}^2$ by four times OM^2 ; from which is evident that for the two sums named in the theorem, disregarding the *same* quantities not depending on O , the same value is found, namely four times OM^2 , etc.

Finally this observation: it is not our purpose to emphasize even in the slightest degree the above-mentioned theorem, up till now accidentally remained unnoticed. Neither have we in view to point out that for each parallelotope P_n the diagonals and the sides furnish equal sums of squares and that all possible relations between diagonals mutually can be represented in the above mentioned form. Whilst referring for this to a paper, to appear shortly in the "Archives Teyler", we repeat here, that this short communication was given to satisfy the wish to show also to non-professional mathematicians by means of a simple example how the study of polydimensional geometry may lead i. a. to the discovery of new theorems of plane or solid geometry.

Chemistry. — "*On the atomic weight of Antimony.*" By Prof. ERNST COHEN and Mr. TH. STRENGERS. (Communicated by Prof. W. H. JULIUS).

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

1. In connection with a physico-chemical study on the nature of so-called *explosive antimony* conducted by one of us (C.) conjointly with Dr. W. E. RINGER, the question of the exact atomic weight of antimony became a very important one.

Notwithstanding a number of investigators¹⁾ have attempted to determine this atomic weight, it is not as yet known with sufficient certainty.

CLARKE²⁾ sums up his criticism on the determinations made up to the present with these words: ". . . . This result, therefore, should be adopted until new determinations of a more conclusive nature, have been made."

¹⁾ BERZELIUS, POGGEND. Annalen **8**, 1 (1826); KESSLER, *ibid.* **95**, 215 (1855); SCHNEIDER, *ibid.* **98**, 293 (1856); ROSE und WEBER, **98**, 455 (1856); DEXTER, *ibid.* **100**, 363 (1857); DUMAS, Annales de chimie et de physique (3), **55**, 175 (1859); KESSLER, Pogg. Ann. **113**, 145 (1861); UNGER, Archiv der Pharmacie **197**, 194 (1871); COOKE, Proc. Amer. Acad. **5**, 13 (1877); KESSLER, Ber. deutsche chem. Gesellschaft, **12**, 1044 (1879); SCHNEIDER, Ueber das Atomgewicht des Antimons, Berlin 1880. Journal f. prakt. Chemie (2) **22**, 131 (1880); COOKE, Amer. Journ. Sciences and Arts, May 1880; B. B. **13**, 951 (1880); PFEIFER, Lieb. Ann. **209**, 161 (1881); POPPER, *ibid.* **233**, 153 (1886); BONGARTZ, B. B. **16**, 1942 (1883); G. CL. Friend and EDGAR F. SMITH, Journal Americ. Chemical Soc. **23**, 502 (1901).

²⁾ The constants of nature, Smithsonian Miscellaneous Collections Part V, Washington 1897.

2. POPPER¹⁾, under VON PEBALS guidance has tried to make a determination of the atomic weight by an electrical method.

He connected in the same circuit a silver coulometer and a cell containing a hydrochloric acid solution of antimony trichloride. A rod of pure antimony (wrapped in linen) suspended in the liquid constituted the positive electrode, whilst the negative electrode consisted of a weighed platinum wire.

During the electrolysis the electrolyte was kept in continual motion by means of a stirrer so as to exclude local changes in the concentration of the liquid.

Under these circumstances explosive antimony is deposited on the negative electrode²⁾. POPPER fused the substance formed in a tube made of hard glass in an atmosphere of nitrogen; in this way the antimony trichloride present in the metallic mass was expelled. As soon as all the chloride had volatilized the antimony regulus was washed first with solution of tartaric acid, then with water, dried at 120° and weighed. Additional experiments had proved that the glass tube did not suffer any alteration in weight on heating and melting the metal contained therein.

The silver electrode in the coulometer was wrapped in a piece of linen. After the electrolysis was completed, the silver which had deposited in the platinum dishes employed was boiled and washed with water until this no longer gave a reaction with hydrochloric acid and it was then dried at 120°.

POPPER's results obtained in the electrolysis of solutions containing respectively 7 and 22 per cent of SbCl_3 are given in the subjoined table. We have, however, recalculated the data as POPPER still uses the atomic weight 107.66 for silver whereas more accurate investigations have shown this to be 107.93.

In a second series of experiments in which a few more improvements had been made as regards the insulation of the silver coulometer, POPPER found for 7 per cent solutions as equivalent weight the value 40.33, therefore as atomic weight the value 120.99.

As he could not discover any sources of error in his process and still believed in the accuracy of the results obtained by COOKE, who, by purely chemical means, had found the atomic weight of antimony to be 119.9 he concludes his paper with the words: "Sollte nicht die Entdeckung des Elements "Germanium" durch WINKLER den

¹⁾ Compare 1.

²⁾ Such was the case with solutions containing 22 per cent of SbCl_3 . In solutions containing 7 per cent. POPPER obtained crystalline *non*-explosive antimony. I will fully refer to this particularity later on in my paper with Dr. RINGER. (COHEN.)

Grams of Sb Cl ₃ in 100 Grains solution.	Weight of the metal deposited in the same time circuit in the same time.		Electrolytic equivalent of Antimony (Silver = 107.93)	Atomic weight.
	Antimony	Silver		
7	4.4788	3.9655	40.25	120.75
7	2.0074	5.3649	40.39	121.47
7	4.1893	11.1847	40.43	121.29
7	4.1885	11.1847	40.42	121.26
7	5.6869	15.1786	40.43	121.29
7	5.6991	15.1786	40.46	121.38
22	4.4856	3.9655	40.43	121.29
22	2.0120	5.3649	40.47	121.41
22	3.8882	10.3740	40.45	121.35
22	3.8903	10.3740	40.47	121.41
22	4.2740	11.3868	40.48	121.44
22	4.2752	11.3868	40.52	121.56

Weg andeuten, auf welchem die Lösung des vorliegenden Rätsels zu suchen sei?"

3. We have not only repeated the research of POPPER but also extended the same by using hydrochloric acid solutions of SbCl₃, whose concentration varied between 2.3 and 83.3 percents of SbCl₃ by weight.

It was necessary to pay particular attention to the purity of the materials employed. The antimony trichloride was obtained from MERCK; 20 grams were dissolved in solution of pure tartaric acid and then digested on the waterbath for some hours with excess of clear sodium sulphide. The liquid remained perfectly clear¹⁾.

Some kilos of this antimony chloride were precipitated with sodium carbonate free from foreign metals, the precipitated Sb₂O₃ was washed, dried and reduced to metal by fusion with pure potassium cyanide in a PERROT's furnace. The crucibles used were previously tested to see whether they would yield any foreign metal to potassium cyanide but we could not prove the presence of any impurity in the melt.

¹⁾ As commercial antimony generally contains lead whose atomic weight exceeds that of antimony it was absolutely necessary to prevent the possibility of any lead being present in the materials employed.

The fused metallic antimony was poured into cylinders of asbestos paper tied round with copper wire: the rods of antimony thus formed were cleansed with hydrochloric acid and washed.

By way of control we dissolved a piece weighing 20 grams in pure strong nitric acid with addition of 75 grams of crystals of tartaric acid. The clear acid solution so obtained was rendered alkaline by adding small lumps of sodium hydroxide prepared from metallic sodium (the lye was free from foreign metals) and digested on the waterbath with a clear solution of sodium sulphide but gave no precipitate.

The solutions were prepared by weighing the pure antimony trichloride roughly and dissolving the same in pure hydrochloric acid of 1.12 sp. gr. at 15°. The exact composition of the solutions was determined by electrolysis of the liquid in presence of sodium sulphide according to NEUMANN'S directions¹⁾.

4. In each experiment two silver coulometers were put into the circuit; one in front and one behind the series of antimony solutions which took part in the electrolysis. The coulometers consisted of 200 cc. platinum dishes with rough inner surfaces. We will not omit to point out that such dishes are particularly suited for coulometric determinations as it is possible to precipitate in them a large amount of silver with little chance of any traces being detached on washing the precipitates²⁾. The amount of silver deposited in our experiments varied from 25 to 50 grams whilst when using the smooth dishes usually employed it is difficult to handle a few grams without loss.

As electrolyte we used a 10 or 15 per cent neutral solution of silver nitrate; no difference was noticed with these solutions. The positive silver plates were cast of silver which we received from Dr. HOITSEMA, Comptroller-general at the local Government Mint. On analysis, we could not trace foreign metals in 100 grams of this silver. The plates were 6.5 c.m. in diameter and 4 mm. thick. They were surrounded by a covering of filter paper (SCHLEICHER and SCHULL). Each silver plate was suspended by a thick platinum wire. The coulometer dishes after being filled with the silver solution were covered with a glass plate with a hole in the centre through which a platinum wire was introduced.

²⁾ Analytical Electrolysis of Metals, Halle 1897. S. 145.

Here, we provisionally took the atomic weight of antimony to be 120; as will be seen from what follows, the uncertainty of the atomic weight is of no consequence *here*.

³⁾ Compare KAHLE. WIED. Ann. 67, N.F. 1 (1899); RICHARDS, COLLINS and HEIMROD, Proc. American Acad. of Arts and Sciences XXXV, 123 (1899). RICHARDS and HEIMROD, Zeitschr. f. physikalische Chemie 41, 302 (1902).

Great care was bestowed on the insulation of all the apparatus. The conducting wires were strongly insulated and were, as far as possible, in contact with air only. Each platinum dish was placed on a copper plate which stood on a glass plate; the latter was carried by porcelain insulators which acted as feet.

For a rough orientation a technical ammeter was included in the circuit; the current was taken from 1 to 3 storage cells.

5. The antimony solutions which were subjected to electrolysis were contained in spacious beakers (1 litre) (*B* in fig. 1) in which constant stirring could take place by means of WITT's centrifugal stirrers. A HEINRICI hot-air motor kept all the stirrers in motion. The rods of antimony which served as positive electrodes were surrounded by a piece of linen which was fixed to the rod with platinum wire, or by glass tubes closed at the lower end containing a large number of not too small perforations (*O, O, O...*) (3 or 4 m.m.). The object of surrounding the rods was to prevent any loose particles of antimony from getting into the liquid.

As negative electrodes we used platinum wires (*P*) about 10 cm. in length and 0.3—0.4 mm. thick; they were provided at the upper end with the capillar glass pieces (*C*), on which a number was engraved.

Both antimony rods and platinum wires were attached to copper binding screws which moved along glass standards (*S*). In order to prevent contamination of the liquids by contact with copper, a piece of platinum wire (*Pt*) was placed between the binding screws and the rods of antimony or platinum suspended thereby.

6. The experiments were now conducted as follows: After the platinum wires had been weighed they were put in their places; the silver coulometers were connected up and the current closed. At the commencement the strength of the current may only amount to a few hundredths of an ampère; if this is exceeded, evolution of hydrogen instead of separation of antimony takes place. When the precipitate on the platinum wires had reached a certain quantity, when in other words, the surface had become enlarged the strength of the current was increased and gradually raised to about 0.3 ampère.

At the end of the electrolyses the rods were rinsed with a 12 per cent solution of tartaric acid ¹⁾, then washed with water, alcohol and ether and dried over sulphuric acid in a desiccator.

¹⁾ By a special experiment we had convinced ourselves that this did not cause any perceptible diminution in weight.

To determine the amount of antimony separated by the current the following method was adopted ¹⁾.

The rod was placed in a tube of hard Jena glass closed at one end (length of the tube 30 cm., diameter 1 cm.). This tube had been previously cleaned, strongly heated in a current of dry air (dried over H_2SO_4 and P_2O_5) and then weighed. The antimony rod was now weighed and by way of control the tube and rod were again weighed together.

The air from the tube was now expelled by means of a continual stream of carbon dioxide which had been dried over sulphuric acid and phosphoric anhydride. The tube (*explosion-tube*) was then closed with a properly fitting india-rubber cork and put into a metal cooling vessel made of composition tube in the manner represented in fig. 2. This tube was connected with the water tap.

If now the explosion tube is shaken for a moment the explosive antimony explodes. The tube is then strongly heated with a triple burner on the spot containing the rod; the $SbCl_3$ evolved condenses on the cold wall of the tube to a clear white mass. The heating is continued until the antimony is perfectly fused and this is then allowed to cool slowly. The tube is then opened, the $SbCl_3$ is removed by rinsing with a mixture of alcohol and ether (3 : 1) the tube is then rinsed with ether and dried by heating in a current of dry air as described above.

The tube with the antimony regulus is now weighed.

A previous experiment had proved that the explosion tube suffers no alteration in weight by the heating and subsequent treatment. It was found for instance that an explosion tube weighed 29.6614 gram before the experiment and 29.6610 gram after the experiment the contents having been removed by means of nitric and tartaric acids.

By way of illustration one of the experiments is reproduced in detail whilst the results of the other measurements are united in a table.

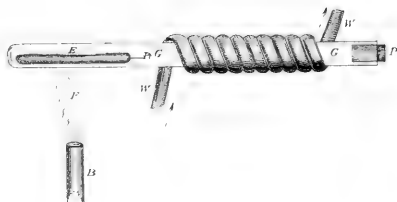
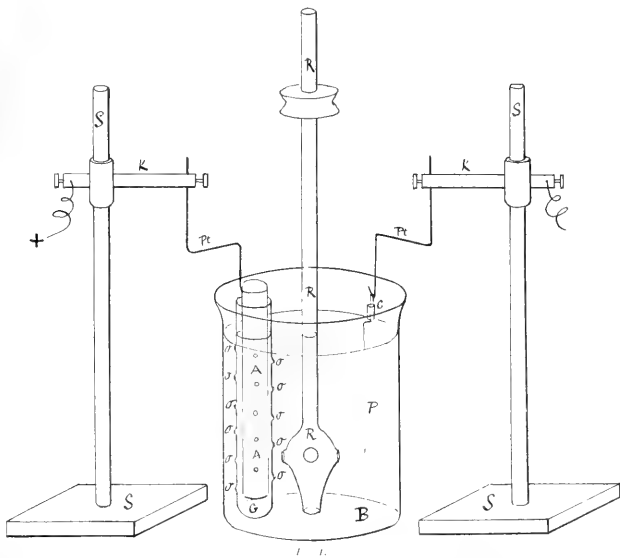
Electrolysis of a 15.6 proc. $SbCl_3$ solution.

Silver coulometer N^o. 1.

weight of platinum dish + silver	73.1920 grams
" " "	36.7310 "
	36.4610 grams

¹⁾ Further particulars about this method will be found in the paper of COHEN and Dr. RINGER.

H
c
O
+



Silver coulometer N^o. 2.

weight of platinum dish + silver	71.4530 grams
" " "	34.9902 "
	weight of silver 36.4628 grams
weight of explosiontube + regulus + platinum wire	55.0281 grams
" " "	41.0780 "
	weight of regulus + platinum wire 13.9501 grams
	weight of platinum wire 0.2696 "
	weight of regulus 13.6805 grams

From this result the equivalent weight of the antimony is calculated as follows:

$$\frac{107.93}{36.4628} \times 13.6805 = 40.49.$$

The results so obtained are collected in the following table. (p. 550).

From this table we see that the atomic weight obtained increases with the concentration of the SbCl_3 solutions and varies between 120.87 and 121.89 within the concentrations 2.3 and 83.3 per cent.

From this it is quite plain that we cannot arrive at the determination of the atomic weight of antimony by the electrolysis of solutions of antimony trichloride and that the values found by POPPER, to which in the calculation of the atomic weight is attached the same value as to those of SCHNEIDER, COOKE and BONGARTZ¹⁾, are quite accidental, being dependent on the concentration of the solutions employed.

It further appears from the above that unknown electrolytic or chemical changes play a part here which require further investigation and which may be expected to add to our knowledge of the formation and composition of the remarkable explosive antimony.

We hope, shortly, to investigate these changes.

¹⁾ Compare OSTWALD, Lehrbuch der allgemeinen Chemie I, 53 (1891).

Grams of Sb Cl ₃ in 100 grams solution.	Weight of the antimony regulus in grams.	Weight of the silver in the Coulometer in grams.		Equivalent weight of the Antimony.	Atomic weight of the Antimony.
		N ^o . 1.	N ^o . 2.		
2.3	16.8747	45.2069	45.2019	40.28	120.87
2.3	14.5914	39.0805	39.0816	40.29	
3.1	18.7961	50.3791	50.3860	40.26	120.78 ¹⁾
5.0	16.9175	45.2019	45.2069	40.38	121.17
5.0	14.6298	39.0805	39.0816	40.39	
5.3	18.8627	50.3791	50.3860	40.40	121.20
5.3	12.6206	33.7224	33.7203	40.38	
5.3	15.0054	40.0810	40.0794	40.41	
14.4	13.1219	33.9633	34.9680	40.49	121.41
14.4	18.8881	50.3791	50.3860	40.46	
14.4	12.6470	33.7224	33.7203	40.47	
15.6	9.5049	25.3416	25.3407	40.48	121.47
15.6	13.6805	36.4610	36.4628	40.49	
15.6	13.6803	36.4610	36.4628	40.49	
18.8	13.5984	36.2088	36.2094	40.53	121.59
18.8	13.8618	36.9531	36.9566	40.53	
52.2	14.6212	38.9046	38.9098	40.56	121.71
52.2	15.0689	40.0810	40.0794	40.58	
55.7	13.7122	36.4610	36.4628	40.58	121.77
55.7	14.7014	39.0805	39.0816	40.59	
83.3	13.6305	36.2088	36.2094	40.63	121.89
83.3	14.9424	—	39.6998	40.61	
83.3	13.8998	36.9531	36.9566	40.64	

¹⁾ This result is decidedly too low, as a trace of antimony got lost during the washing.

Chemistry. — “*The conductive power of hydrazine and of substances dissolved therein.*” By Prof. ERNST COHEN and Prof. C. A. LOBRY DE BRUYN. (Communicated by Prof. C. A. LOBRY DE BRUYN).

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

The investigation of the conductive power of non-aqueous solutions has of late years been known to have an increasing significance and particularly so on account of the important result that the laws and rules applying to aqueous solutions do not appear to apply in the case of other solvents. Apart from methyl and ethyl alcohol (the constitution of which does not differ much from the type water) sulphurdioxide, ammonia (NH_3), formic acid, hydrocyanic acid, pyridine, some nitriles, hydrogen peroxide and others have been studied as such¹).

The physical properties of free hydrazine²) N_2H_4 although still incompletely known, might lead us to suppose that this liquid would manifest a strong ionising power. In the first place, like water, the lower alcohols and acids, it possesses an abnormally high boiling point. This is obvious if this point (about 113° at 760 m.m.) is compared with of ammonia (-34°), difference of 147° , and if one considers that the difference between the boiling points of CH_4 and C_2H_6 is decidedly less (80°); this fact as well as the high critical temperature of (at least) 380° point to an association of the N_2H_4 molecules. The solubility of several alkali salts in hydrazine has also been shown to be very considerable although less than in water. Another existing observation points to the fact that hydrazine may, like ammoniac take the place of water of crystallisation³). And finally, the dielectric constant of hydrazine, which Prof. P. DRUDE (Giessen) had the kindness to determine at our request, has turned out to be rather high, namely, 53 at 22° . It is now a known fact that there exists a certain although sometimes remote parallelism between the dissociating power of a liquid on the one hand and the association of its molecules, the solvent power and the dielectric constant on the other hand. As according to the experiments of FRANKLIN and KRAUS and of CADY liquefied ammonia is an ionising solvent, this might also be expected in the case of hydrazine. From the experiments⁴) presently to be described it will be seen that such is the case.

¹) Compare JONES, Am. Ch. J. **25**. 232. KAULENBERG, J. Phys. Chem. **5**. 339. WALDEN and CENTNERSZWER, Z. phys. Ch. **39**. 514, 557 e. by J. TRAUBE, Chem. Zt. **26**. 1071. (1902).

²) LOBRY DE BRUYN, Recueil des Travaux Chimiques des Pays-Bas. **15**. 174.

³) Ibid. 179.

⁴) Some preliminary determinations were already made in 1896. l. c. 179.

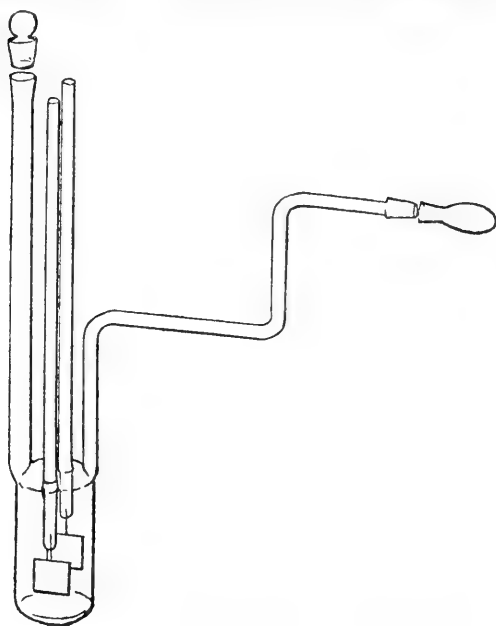
Let us first observe that the dielectric constant of hydrazine is only surpassed by those of five other liquids and is decidedly larger than that of NH_3 . We have namely:

hydrocyanic acid	95	acetonitrile	40
hydrogen peroxide	93	nitrobenzene	36.5
water	82	methylalcohol	32.5
formic acid	57	ammonia	22 (at -34°)
nitromethane	56.5	pyridin	20
hydrazine	53		

The peculiar properties of hydrazine (its very hygroscopic nature and liability to oxidation by atmospheric oxygen) demand great precautions in its preparation. It took place, according to the method already described¹⁾, by treatment of the so-called hydrate with barium oxide and distillation in an atmosphere of hydrogen.

The heating with barium oxide and subsequent distillation were thrice repeated and the base was finally collected in six different fractions in pipette-shaped tubes in the manner previously described. During the last distillation the base had been only in contact with purified, dry hydrogen.

Apart from the properties of hydrazine mentioned, the high cost of the material was a factor which in our experiments had to be taken into account. A special apparatus (see illustration) was, therefore constructed which admitted of working with a small quantity of the base



(about 5.5 c.c.) and through which pure, dry nitrogen²⁾ could be passed, whilst through the exit tube for the gas the weighed portions of the different salts could be introduced.

On account of the somewhat limited quantity of the base at disposal we could not, as is customary in the determination of the conductive power of solutions, start with the largest concentration and successively dilute this by adding the solvent, but the reverse was to be done.

¹⁾ l. c. p. 175.

²⁾ We take the opportunity to call attention to the fact that platinised electrodes

Weighed quantities of a salt were, therefore, successively dissolved; on account of the unavoidable errors in weighing it was difficult to experiment with very dilute solutions of accurately known composition, but by evaporating a measured quantity of a very dilute aqueous solution in a pipette which was then rinsed with the hydrazine we have reached for KCl a concentration of $V = \pm 900$.

In view of the above we wish to remark generally that our results cannot lay claim to very great accuracy, although they quite suffice even from a quantitative point of view, to prove that free hydrazine has a strong ionising power comparable with that of water.

We have worked with solutions of H_2O , KCl, KBr, and KJ and made a few experiments with a solution of Na and H_3N in $N_2 H_4$.

In the first experiment the six different fractions of the hydrazine had not been kept separate; as we had previously found ¹⁾ that the meltingpoints of the second and fourth fractions were the same we thought we might conclude that at least the middle fractions were similar. It then appeared, however, that the conductive power of the bases taken from different tubes often showed appreciable differences.

For this reason a second preparation was made and the hydrazine of each fraction (each time collected in several tubes) was examined separately as to its conductive power. From the following figures it appears that the conductive power gradually decreases and is smallest for the last fraction.

fraction n ^o . 2	κ at 25° = 18.110 ⁻⁵
3	12.8 "
4	11.2 "
5	10.0 "
6	6.5 "

We do not know what impurity (in any case very small) is the cause of this; possibly we are dealing here with a minute quantity of ammonia which is present in largest amount in the first fractions

The smallest conductive power observed by us in any fraction prepared previously was 4.10⁻⁵.

Our experiments have been mostly conducted with fraction N^o. 6 of the above-mentioned quantity.

dried in the air may occlude such an appreciable amount of oxygen that this must make its influence felt when working with readily oxidisable liquids. Such appeared to be the case when filling our apparatus with hydrogen when a spontaneous deposit of visible drops of water was formed.

²⁾ Prepared from air and phosphorus.

¹⁾ l. c. p. 177.

The apparatus was put into a glass vessel containing paraffin oil which was placed in an Ostwald thermostat; the temperature was 25°.

Hydrazine and water ($t = 25^\circ$)			
5 ^e fraction.	$G = 5.185.$	6 ^e fraction.	$G = 4.249.$
N.	α	N	α
0	$10.0 \cdot 10^{-5}$	0	$6.04 \cdot 10^{-5}$
0.93	9.79 »	41.4	4.71 »
7.94	8.95 »	49.5	4.5 »
21.45	7.68 »	58.4	4.36 »
33.8	7.22 »	69.5	4.55 »
65.6	6.04 »	81.6	4.9 »
82.4	6.09 »	124.7	7.3 »
101.8	7.85 »		
156	10.51 »		
255.5	17.51 »		

Potassiumchloride.

$t = 25^\circ$				
		$\alpha = 6,2 \cdot 10^{-5}$		
G	g	V	α	Λ^1
5.369	0,0272	44.7	$7.0 \cdot 10^{-3}$	102.9
»	0,0157	25.4	4.2 »	103.7
»	0,0080	49.7	2.2 »	109.3
[± 5.4	0,00045	± 900	$1.2 \cdot 10^{-4}$	[$\pm 107^2$)]

Potassiumbromide.

$t = 25^\circ$				
		$\alpha = 6,5 \cdot 10^{-5}$		
G	g	V	α	Λ
5.350	0,0617	40.3	$10.05 \cdot 10^{-3}$	103.8
»	0,0329	19.3	5.66 »	109.2
»	0,0214	29.9	3.77 »	112.7
»	0,0105	60.7	1.965 »	118.9

¹⁾ Λ_∞ could not be determined, so that the degree of dissociation of the salts is not known. The Λ 's, however, agree in magnitude with those of the aqueous solutions of the same salts.

²⁾ This value, obtained in the manner described on p. 553, is as a matter of fact uncertain. It proves that a very minute quantity of a dissolved substance may increase the conductive power considerably.

Potassiumiodide.

$t = 25^\circ$		$\alpha = 5,6.10^{-5}$ N_2H_4		
G	g	V	α	Λ
5.600	0,072	42.9	$8.49.10^{-3}$	105.6
»	0,0493	48.8	5.79 »	108.8
»	0,0280	33.2	3.40 »	112.8
»	0,0129	72	4.64 »	118

G = weight of hydrazine in grams.

Λ = equivalent conductive power.

g = weight of the salt in grams.

V = number of Liters, in which is dissolved one mol. of the substance.

α = specific conductive power

α for the water used = $0,28.10^{-5}$

Without committing a grave error the sp. gr. of hydrazine at 25° may be taken as 1.00.

It is already known that sodium dissolves in hydrazine with evolution of hydrogen¹). Pure hydrazine ($\alpha=9,1.10^{-5}$) was introduced into the apparatus and two particles of sodium (weighing about 10 milligrams) were added.

The metal slowly dissolved with evolution of hydrogen and after solution was complete the specific conductive power appeared to have increased to 131.10^{-5} .

It seemed very peculiar that a powerful evolution of gas still went on after the sodium had dissolved, showing a decomposition of the hydrazine with formation of ammonia. This decomposition ceased as soon as the liquid was poured out of the apparatus; apparently it only takes place by contact with the platinum black present on the electrodes and is, therefore, quite comparable to the spontaneous decomposition of an alkaline solution of hydrogen peroxide exposed to the same influence.

Finally a few experiments were made with a solution of ammonia in hydrazine. The solubility of that gas at the ordinary temperature did not seem to be large; about 4.3 per cent of NH_3 is present in the saturated solution. After a few bubbles of ammonia had been absorbed in the hydrazine (with $\alpha = 5.2.10^{-5}$) the conductive power appeared to be but slightly increased ($\alpha = 6.9.10^{-5}$); this was also still the case after the liquid had been saturated with ammonia (about

¹) l. c. p. 183. Dr. J. W. DITO has found that an atom of hydrogen is replaced here; the NaH_3N_2 formed is a substance which on being exposed to the air causes a violent spontaneous explosion.

220 mgr. of H_3N in 4.920 gr. of N_2H_4 , $v = 0.38$, $\alpha = 9.10^{-5}$). It is known that on dissolving ammonia in water the conductive power is but very slightly increased.

From the foregoing we may draw the conclusion that, with regard to its ionising power, hydrazine is comparable to water.

As regards mixtures of hydrazine and water it may be observed that on addition of water the conductive power at first decreases reaching a minimum with a mixture of 60 mols. of H_2O to 100 mols. N_2H_4 (about 25 per cent of H_2O and 75 per cent of N_2H_4) then increasing again. This minimum, therefore, does not correspond with the composition $\text{N}_2\text{H}_4 + \text{H}_2\text{O}$, or the so-called hydrate.

Utrecht—Amsterdam, January 1903.

Chemistry. — “*The velocity of transformation of tribromophenol-bromine into tetrabromophenol.*” By MR. A. H. J. BELZER ¹⁾. (4th Communication on intramolecular rearrangement, presented by Prof. C. A. LOBRY DE BRUYN).

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

BENEDIKT ²⁾ found in 1879 that tribromophenol brought into contact with bromine water is capable of exchanging a fourth hydrogen atom for bromine with formation of a tetrabromo-derivative. The study of this substance led him to the conclusion that one Br-atom occupies a peculiar position in the molecule; it is, in fact, the cause of a certain number of reactions in which that Br-atom is readily displaced. As moreover the new substance seemed to have lost the character of a phenol as shown by its insolubility in alkalis, BENEDIKT gave it the formula $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{OBr}$ and the name of tribromophenolbromine. BENEDIKT also noticed that, when melted under sulphuric acid, it passes into the already known isomeric tetrabromophenol, a true phenol which no longer contains a loosely bound Br-atom.

In his first publication BENEDIKT looked upon this transformation into tetrabromophenol not as an intramolecular displacement of atoms but as a process taking place between two mols. of tribromophenolbromine; in a later communication however he does so, without stating any reasons.

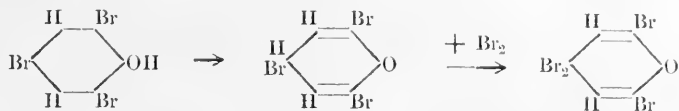
When a few years ago, JOH. THIELE ³⁾ found that BENEDIKT'S

¹⁾ Proc. 31 May, 28 June and 25 Oct. 1902.

²⁾ Annalen **199**. 127, Monatshefte **1**. 361.

³⁾ Ber. **33**. 673 (1900).

tribromophenolbromine by means of leadacetate passed into 2,6-dibromoquinone, with substitution of 2 Br by O, he looked upon it as a dibromoquinone in which one O is replaced by 2 Br [therefore as a tetrabromoketodihydrobenzene]; he is of opinion that its formation from tribromophenol can only be explained by assuming that the latter can react in the tautomeric form of a p-quinoid ketone as follows:



In a paper which appeared a year ago, KASTLE¹⁾ has come to the same conclusion as THIELE, as the result of investigations conducted conjointly with LOEVENHART, ROSA SPEIJER and GILBERT. KASTLE has also established the fact that it is only sulphuric acid which, even at the ordinary temperature, is capable of causing the transformation into tetrabromophenol; a dozen other reagents gave a negative result. In order to explain this specific action of sulphuric acid, KASTLE assumes the intermediate formation of an additive product of this acid with tribromophenolbromine; this at first would lose HBr₁ which would then again react at once with reformation of sulphuric acid and cause the migration of Br into the benzene nucleus. This interpretation of the transformation requires the appearance of two non-isolated and therefore hypothetical intermediate products and of three successive reactions.

Mr. BELZER has now studied the velocity of transformation of tribromophenolbromine. The circumstance that the first substance readily parts with an atom of bromine would lead to expect that its quantitative estimation would be possible in the presence of tetrabromophenol. It now appeared that the elimination of free iodine from hydriodic acid, also observed by KASTLE, takes place quantitatively; tribromophenolbromine may therefore be estimated in the presence of tetrabromophenol by titration.

At the commencement of the investigation the behaviour of the solid substance towards sulphuric acid was ascertained. If the crystals are covered with the ordinary 96 per cent acid it is noticed that they lose their yellow colour and become opaque and white; on solution in the acid taking place nothing can be perceived even by the aid of the microscope. No formation of striae can be observed; the whole phenomenon seems to be enacted within the solid substance commencing on the surface where the substance is in contact with

¹⁾ Amer. Ch. J. 27. 31. (1902).

the acid. If the velocity of transformation is measured under these circumstances it is no matter for surprise *firstly* that no reaction constant is found, *secondly* that the reaction coefficient constantly diminishes as the inner parts of the crystals get more and more inaccessible to the acid. As expected beforehand the experiment has shown that very small crystals or the powdered substance are, on account of the larger free surface, more rapidly transformed than the larger crystals. The continuation of the research will show that the transformation is monomolecular and must, therefore, be taken as a real displacement of atoms (perhaps of two displacements one of which takes place with very great velocity). It is a remarkable fact that there should take place inside the molecule of a solid substance a displacement of atoms, an internal change of equilibrium leaving the molecule intact, by mere contact with sulphuric acid, without there being any question of solution.

Although we could not expect to get reaction-constants for a heterogenous mixture of a solid substance and sulphuric acid, this should be duly the case when we worked in a solvent. Here however a difficulty occurred which at first threatened to put a stop to the further prosecution of the research. A solvent was wanted which had no action either on tribromophenolbromine or sulphuric acid. Acetic acid scarcely dissolved the first substance and chloroform appeared to dissolve only traces of 96 per cent sulphuric acid. It was finally decided to choose the latter solvent and to thoroughly shake the solution with sulphuric acid ¹⁾. The experiment proved that on applying the formula of the first order, constant reaction-coefficients made their appearance. A first result was thus obtained; the transformation does not proceed bimolecularly.

Mr. BELZER has now studied the influence of the concentration of the sulphuric acid and the temperature.

In most of the experiments, 3 grams of the substance were dissolved in 150 cc. of pure chloroform ²⁾, the solution strongly shaken with the acid and after definite times 25 cc. were titrated.

Use has been made of:

- a.* H_2SO_4 with about 36% SO_3 , *b.* H_2SO_4 with about 1% SO_3
c. equal volumes of *b* and *d.* *d.* 96 per cent H_2SO_4 .

In the following tables the results obtained are not given in the form of reaction-constants, but to make the matter more plain, the

¹⁾ A uniform emulsion is very soon obtained.

²⁾ The chloroform was agitated a few times with water, dried over calcium-chloride, shaken with strong sulphuric acid and redistilled; it was preserved in the dark.

times (T) are mentioned at which the transformation has proceeded halfway.

A. Influence of the Concentration of Sulphuric Acid.

$t = 25^\circ$. 0,5 cc. sulphuric acid.

	acid a	b	c	d
T.	5 min. 49 sec.	2 hours 57 m.	13 h. 40.5 m.	very slowly

$t = 25^\circ$. 1 cc. sulphuric acid.

	acid a	b	c	d
T.	too rapid	25 m. 44 s.	2 h. 38.5 m.	7 h. 45 m.

B. Influence of the Quantity of Sulphuric Acid.

$t = 25^\circ$. acid a.

	1 cc.	0.6 cc.	0.5 cc.	0.3 cc.
T.	too rapid	too rapid	5 m. 49 s.	3 h. 8 m.

$t = 25^\circ$. acid b.

	2 cc.	1.5 cc. ¹⁾	1.25 cc.	1 cc.	0.5 cc.	0.25 cc. ²⁾
T.	too rapid	too rapid	25 m. 44 s.	55 m. 20 s.	2 h. 57 m.	

$t = 25^\circ$. acid c.

	1.5 cc.	1 cc.	0.5 cc.
T.	1 h. 16 m.	1. 2 h. 32.4 m. 2. 2 h. 38.4 m.	13 h. 40.5 m.

C. Influence of the Temperature.

Acid a.

	0.5 cc.	0.3 cc.	0.2 cc.
T. at $t = 35^\circ$	---	6 m. 12.5 s.	32 m. 33 s.
» 25°	5 m. 49 s.	3 h. 8 m.	---
» 15°	58 m. 45 s.	---	---

$\left. \begin{array}{l} \pm 30 \\ \pm 10 \end{array} \right\} \text{times}$

Acid b.

	1 cc.	0.5 cc.
T. at $t = 35^\circ$	---	33 m. 56 s.
» 25°	25 m. 44 s.	2 h. 57 m.
» 15°	1 h. 1.5 m.	---

$\left. \begin{array}{l} \pm 4 \\ \pm 2 \end{array} \right\} \text{times}$

¹⁾ Transformation almost completed after 20 minutes.

²⁾ Not yet decomposed to the extent of 15 % after 21 hours.

	Acid c, 1 cc.	Acid d. 1 cc.
T. at $t = 35^\circ$	58 m. 10 s.	1 h. 53.6 m.
» 25°	2 h. 35 m.	7 h. 45 m.
» 45°	3 h. 27 m.	

From the results obtained it appears in the first place that the transformation is a monomolecular one and, taking into consideration the circumstances under which it takes place, must be considered as an intramolecular rearrangement of atoms.

To this conclusion the following observations may be added.

A. The influence of the concentration of the acid, the other circumstances being the same, is very great. The course of the figures leads to the idea that the active agent, the catalyser is not H_2SO_4 but SO_3 . Experiments were therefore made to ascertain how chloroform behaves towards the four acids employed. Whilst from ordinary 96 % acid (*d*) but very minute traces were dissolved, this amount was perceptibly larger with acid *c* and still larger with acid *b*, whilst acid *a* appeared to yield very much SO_3 to the chloroform¹⁾.

The idea that SO_3 is the catalysing substance is consequently confirmed. The rapid decrease of the concentration of the acid is also in agreement with this idea; this velocity is therefore as it were a measure of the concentration of the SO_3 still present in a sulphuric acid of given concentration.

B. It is now also very plain that the quantity of the acid must have a great influence. As shown by its behaviour to acid *a*, chloroform may dissolve considerable quantities of SO_3 . On shaking with sulphuric acid of a lesser concentration, the amount of SO_3 which passes into the chloroform will consequently depend on the quantity of the acid. The equilibrium for the SO_3 which distributes itself between the chloroform and the sulphuric acid changes, as is known, with the relative quantities of the two liquids and with the temperature.

As a consequence of the view taken here, it must be assumed that ordinary 96 % sulphuric acid still contains a minute quantity, of free SO_3 -molecules. This view is admissible²⁾ since it is known

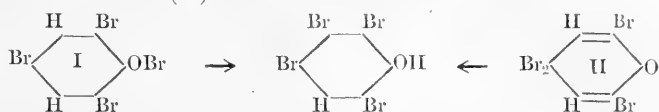
¹⁾ The ratio in which different acids yield SO_3 to chloroform will be further determined.

²⁾ KNIETSCH, in his well-known research on sulphuric acid, has shown that an acid of 97–98 % absorbs SO_3 much more readily than acids of smaller or larger concentration. From the results obtained up to the present it does not appear that, in the transformation of tribromophenolbromine, the 98 % acid *c* behaves in a particular manner; an extension of the research will elucidate this question.

that 100 % sulphuric acid contains a little SO_3 and consequently free H_2O .

C. The temperature-coefficient for sulphuric acid *a* is particularly large and increases rapidly with the temperature; for acid *b* it is decidedly smaller and very small for the 96 % acid. It will be readily understood that in the case of the acid *a* the dissociation of H_2SO_4 into SO_3 and H_2O and the distribution of SO_3 between chloroform and sulphuric acid are modified in a large degree when a change of temperature takes place.

The rearrangement of atoms may now be represented by the following schemes which respectively correspond with BENEDIKT's formula (I) and THIELE's formula (II):



Against the acceptance of THIELE's formulè (II) it may be pointed out that in the displacement a Br atom must first remove an H atom; this then proceeds to the O atom with migration of the double bonds, a rather intricate process practically consisting of three succeeding displacements. As it has been proved that the reaction is one of the first order, two of those displacements must take place with immeasurable velocity. Against BENEDIKT's formulè (I) may be remarked that, according to experience, the meta-position is hardly ever selected in the migration of an atom or of groups from the side chain into the nucleus.

The hypothesis proposed by KASTLE, which assumes the intermediate formation and decomposition of non-isolated products, is not at all supported by the observations communicated here.

The investigation as to the transformation of tribromophenolbromine will be completed and also extended to other analogous compounds.

Geology. — "*Some New Under-Cambrian Erratic-blocks from the Dutch Diluvium*". By J. H. BONNEMA. (Communicated by Prof. J. W. MOLL).

I. In the Geological-Mineralogic Institute at Groningen is found a piece of sandstone which a few years ago I found at Odoorn, in the province of Drente. With muriatic acid applied to it, there is no effervescence; consequently it does not contain any calcium-carbonate. The grains of sand are small, but with a magnifying glass they may be well distinguished. They are peculiarly lustrous.

The colour of this erratic-block is chiefly dark-grey. In some

places it is brownish. Moreover there are light-grey worm-shaped parts, varying in length and having a breadth of about 6 millimetres. This erratic-block is most probably a piece of Under-Cambrian sandstone, in which is found one of those problematical things that are sometimes called worm-passages. As they are not straight and do not run parallel to each other, they are different from those described as *Scolithus linearis* Hall. They show more resemblance with those tubes that were described by TORELL¹⁾ as *Scolithus errans* of Hardeberga and Andrarum. According to HOLST²⁾, however, there are various kinds of these worm-passages differing from *Scolithus linearis* Hall, whilst they also occur in different layers. This geologist makes mention of them as being found both in many places in the neighbourhood of Simrishamn and near Kalmar.

The Odoorn erratic-block bears no resemblance to the Hardeberga sandstone, in which *Scolithus errans* TORELL is found. MOBERG³⁾ writes that this sandstone shows a greyish-green colour, and that the worm-passages are dark-coloured. Nor does it resemble the Andrarum (Forsemölla) sandstone. According to TULLBERG⁴⁾ the latter is a white, quartziferous sandstone with yellow worm-passages.

The erratic-block also differs from the "Kråksten", which HOLST mentions, as being found near Kalmar, and which is greenish grey. From the kinds of sandstone with worm-passages which according to HOLST are met with in the neighbourhood of Simrishamn, differs that which occurs to the West of Raskarum in being whitish; and that which is found close by Ljunglyckorna is different because its worm-passages possess a dark colour. The sandstone which, according to this geologist, occurs to the North-West of Raskarum, may resemble, in colour, the Odoorn erratic-block: he says that its colour is sometimes a dirty-grey one. Unfortunately he does not tell his readers what is the colour of the worm-passages.

Consequently we cannot with certainty conclude whether this kind of sandstone still exists as firm rock, or not.

Nor have I been able to find anything whatever concerning the presence of suchlike erratic-blocks in the German and the Dutch diluvium.

¹⁾ TORELL, *Petrificata Suecana formationis cambricae*. Lunds Univ. Årsskrift. 1869. Tom. VI. p. 12.

²⁾ HOLST. *Beskrifning till kartbladet Simrishamn*. Sveriges geologiska Undersökning. 1892. Ser. Aa. N^o. 109, p. 13.

HOLST. *Bidrag till kännedomen om lagerföljden inom den kambriska sandstenen*. Sveriges geologiska Undersökning, 1893. Ser. C. N^o. 130, p. 6, 13, 14.

³⁾ MOBERG. *Geologisk vägvisare inom Fogelsångstrakten*. 1896. p. 30.

⁴⁾ TULLBERG. *Om Agnostus-arterna i de kambriska aflagringarne vid Andrarum*. Sveriges geologiska Undersökning. 1880. Ser. C. N^o. 42, p. 3.

11. Some years ago I made an excursion in the surroundings of Murmerwoude in company with Mr. Botke, at the time a teacher at Murmerwoude, now a teacher at a secondary school at Nimeguen. To the West of this village, situated in the north-eastern part of the province of Frisia, we found in the sand that lay by the side of a freshly-dug canal two slab-shaped pieces of sandstone that fit each other exactly and must have formed one whole. The dimensions of the bigger piece are about 20, 10 and 4,5 centimetres. The other piece also possesses the two first-mentioned dimensions, but the third is 3 centimetres.

These pieces drew my attention as containing many more or less complete stone-kernels and off-prints of pyramidal *Hyolithus*-shells. The pointed ends of all these lie in the same direction, which must certainly be attributed to the influence of streaming water.

These erratic-blocks consist of hard, grey, very fine-grained sandstone. With muriatic acid applied to them there is no effervescence. Here and there they show small, yellow-brown spots. Some of the stone-kernels and that which lies close around them show the same colour.

The stone-kernels are straight and slowly increase in breadth. The dorsal side is flat or somewhat concave; at the mouth it is more or less convex. This side is not lengthened towards the front, so that we have here a specimen of the subgenus *Orthotheca*. With the exception of the dorsal side the surface of the stone-kernels is regularly vaulted. Consequently the transverse section is about circle-shaped, with only one segment cut off. Towards the pointed end they become more or less triangular. In one stone-kernel, which is not exposed to view in its full length, the visible part points to a length of about 35 millimetres and to a breadth, at the mouth, of 7 millimetres.

It appears from these properties that these stone-kernels originate from the *Hyolithus* (*Orthotheca*)-species, which has been described and pictured by HOLM¹⁾ as *Hyolithus* (*Orthotheca*) *de Geeri*.

HOLM tells us already that sandstone with *Hyolithus de Geeri* is Under-Cambrian. I have, however, not been able to find in his work, on what grounds this assertion is founded. Most probably he came to this conclusion because the nature of the stone points to it. At the time sandstone with *Hyolithus de Geeri* was not yet known as firm rock. Even now I have not been able to find in the books at my disposal, that sandstone with *Hyolithus de Geeri* should be known

¹⁾ HOLM. Sveriges Kambrisk-Siluriska Hyolithidae och Conulariidae. Sveriges geologiska Undersökning. Ser. C. No. 112. p. 54.

as such. As far as I can see this species of *Hyalolithus*, when Holm described it, had not been discovered in company with a fossil from which its age might be determined. MOBERG¹⁾ afterward found many specimens in a few big blocks of sandstone, which furnished him the material for the description of the new species of Trilobites called *Holmia Lundgreni*. The latter lay in the neighbourhood of lake Tunbyholm in the eastern part of the province of Schonen; according to MOBERG suchlike stone with remains of Trilobites occurs as firm rock not far from this place. As MOBERG informs us that sandstone with *Holmia Lundgreni* is older than that with *Holmia Kjerulfi* Linns, this was probably also the case with the sandstone-layers of which the Murmerwoude erratic-blocks formerly formed part.

It appears from MOBERG's description of the stone of the erratic-blocks with *Holmia Lundgreni*, that this stone in some respects resembles the material of which the Murmerwoude erratic-blocks consist. Both are very fine-grained and contain no calcium-carbonate. There does not seem to be much difference in colour either, at least as far as some parts of the Swedish erratic-blocks are concerned: MOBERG tells us that the sandstone described by him is chiefly of a bright light-grey colour, though sometimes showing small brown spots of ferrihydroxide. My erratic blocks, however, contain no pieces of phosphorite, which those from the neighbourhood of lake Tunbyholm do.

Besides the erratic-blocks spoken of just now, others of sandstone with *Hyalolithus de Geeri*-remains were also found, as Holm tells us, in the province of Schonen, near Simrishamn and Köpinge.

The same author makes mention of suchlike stones having been gathered near Rüdersdorf not far from Berlin, and near Bützow in Mecklenburg. It follows from the descriptions he gives of these pieces, that petrographically they bear no resemblance to those found at Murmerwoude. The latter are least different from the erratic-block found by Prof. DE GEER at Rüdersdorf. My pieces, however, contain no particles of glimmer.

No more have corresponding erratic-blocks of *Hyalolithus*-sandstone been found in any part of the Netherlands. The first of this kind of stone were made mention of by VAN CALKER²⁾. They originate from Steenberg in the northern part of Drente; they are three stones

1) MOBERG. Sveriges älsta kända Trilobiter. Geol. Fören. in Stockholm förhandlingar 1899. Bd. 21. Häft 4. p. 324.

2) VAN CALKER. Ueber ein Vorkommen von Kantengeschieben und von *Hyalolithus*- und *Scolithus*-Sandstein in Holland. Zeitschr. d. Deutsch. geol. Gesellschaft. Jahrg. 1890. p. 581.

resembling each other. From the description VAN CALKER gives of the stonekernels occurring in them, HOLM already drew the conclusion that they originate from *Hyalolithus de Geeri*. These erratic-blocks consist, however, of dark asch-grey sandstone, so that they differ in colour from the Murmerwoude ones.

Afterward two more pieces of *Hyalolithus*-sandstone were mentioned by me¹⁾. One was found at Kloosterholt (Heiligerlee), the other at Roden, in the North of the province of Drente. The former is a small piece of fine-grained sand-stone, yellow-grey on the inside and brownish on the outside, in which are found some fragments of stone-kernels of *Hyalolithus*-shells. A few of these fragments are entirely dark-brown, others have a light-grey surface. One of the stone-kernels shows the transverse section characteristic of *Hyalolithus de Geeri*. The Roden erratic-block is rather a large slab of sandstone, containing especially off-prints of pyramidal *Hyalolithus*-shells. This one is reddish on the inside and light-grey on the outside.

Where the sandstone-layers of which the Murmerwoude erratic-blocks in former times formed part, were originally found as firm rock, cannot be said with certainty, as appears from what was written above. Most probably it was near the western coast of the southern part of Sweden.

III. That the knowledge of our sedimentary erratics still leaves so much to be desired, must certainly be partly attributed to the fact that so few of them have been gathered up to this time. Non-geologists, too, by their researches, may deserve well of this branch of knowledge, as was proved once more by Prof. Dr. J. C. KAPTEYN, filling a chair at the Groningen University.

This well-known Astronomer, who in summer lives at Vries, in the northern part of Drente, last summer searched the surroundings of this village for sedimentary erratic-blocks. To his researches we owe a piece that is certainly the most interesting of the erratics described here.

Just outside this village, by the road leading to Donderen, was found a small, slab-shaped erratic-block three centimetres thick, the largest dimension of which is 14 centimetres. It consists of sandstone coloured yellow-grey by ferrihydroxide. At the surface it is brownish. With muriatic acid there is no effervescence. The grains of sand

¹⁾ BONNEMA. De sedimentaire zwerfblokken van Kloosterholt (Heiligerlee). Versl. v. d. Koninkl. Akad. v. Wetenschappen 1898. p. 450.

VAN CALKER, Ueber eine Sammlung von Geschieben von Kloosterholt. Zeitschr. d. Deutsch. geol. Gesellsch. Jahrg. 1898. p. 234.

are for the greater part very small; they are not easily distinguished. Among them are bigger transparent ones. The diameter of these latter grains is at most $\frac{1}{2}$ millimetre; they are mostly arranged in parallel planes, in consequence of which an indistinct layer-like construction becomes visible on the vertical sides. On one of the horizontal sides there are still parts of a few thin layers. In the stone are a great many small cavities, which were formerly evidently filled with organic remains.

On both of the horizontal sides we find remains of Tribolites. On one of them the most important are an off-print of a mid-shell about 8 millimetres long, and a stone-kernel 10 millimetres long, part of the shell of which, turned into iron-hydroxide, is still present. On the other horizontal side is found the front part of an off-print of a much larger mid-shell, which once had a length of about 15 millimetres.

Undoubtedly these remains, which in many respects resemble each other, have come from the same kind of Tribolites. The two first mentioned are remains of younger individuals; the other belonged to a more or less full-grown specimen.

With the younger individuals the glabella was convex, its length surpassed its breadth a little, its breadth diminishing towards the front. On the front side the glabella is somewhat rounded. On the plaster-cast I made of the off-print of the small mid-shell, it is clearly visible that the glabella possessed at least 2 side-furrows on either side. The stone-kernel shows that the neck-ring was broadened in the middle. The cheeks were vaulted, which is very clear in the stone-kernel especially. Very characteristic is a deep furrow enclosing the glabella in front and being continued on either side on the cheeks, where it broadens and becomes less deep. Before this furrow is a vaulted part, which does not turn down. The front-edge of this part is on about the same level with the back-edge, whilst its height is equal to that of the glabella. In the off-print of the little mid-shell the glabella is $4\frac{1}{2}$ millimetres in length, and the part in front of it nearly 3 millimetres in breadth.

It is apparent from the off-print of the mid-shell of the more or less full-grown animal, which mid-shell is only partly exposed to view, that the glabella and that part of the mid-shell which is in front of it, which does not turn down here either, are less vaulted, and that the furrow separating the two, is less deep. Here are no side-furrows to be distinguished on the glabella.

With the assistance of the scientific works I dispose of, I found that these remains are most like those of *Arionellus primaevus* BRÜGGER, of which up to this time only mid-shells have been pictured and

described. The first pictures were given by KJERULF¹, after remains of the "grøn skifer" from Tomten (Tömten?) in Norway. He informed us already that they came from an Arionellus-species. Later on they were described by BRÖGGER²), who by them was induced to assume the new species Arionellus Primaevus. Under this head he also ranged the mid-shell that had been pictured by KJERULF in fig. 6. Afterward LINNARSSON³) pictured and described remains of this Tribolite. He moreover tells us that the mid-shell pictured by KJERULF as fig. 6 rather seems to belong to a new species called Ellipsocephalus Nordenskiöldi, instituted by him in the same essay. His material had been got from the "gråvacke-skiffern" of Forsemölla near Andrarum. He dared with certainty to range under the head Arionellus Primaevus a small mid-shell 5 millimetres long, which had been found in a sandstone-like variety of the stone mentioned above. This was not the case with mid-shells from the ordinary stone, which are about 15 millimetres long. He gives as his reasons for not daring to range these latter among Arionellus Primaevus BRÖGGER: first that they are much flatter, secondly that the furrows are much shallower, thirdly that the glabella has no side-furrows, fourthly that the glabella towards the front considerably diminishes in breadth. Why, notwithstanding all this, he at first ranged them under this head, though he had never heard of transition-forms, he explains by saying that BARRANDE had found exactly the same difference between the old and the young specimens of the Bohemian species Arionellus Ceticcephalus Barr., of which transition-forms are known.

The very same points of difference occur in the Trilobites-remains of the erratic-block found at Vries. Here, however, the glabella of the older specimen does not diminish in breadth more considerably than that of the younger individuals.

As I wished to be as certain as possible in my determination, I wrote to Prof. MOBERG, director of the Geological Institute at Lund, to ask whether there was any material for comparison at my disposal there. Remains of this species of Trilobites seem to be very rare at Forsemölla, however, so that my request could not be complied with. I received as a present, however, a mid-shell of the Ellipsocephalus Nordenskiöldi, which seem to occur more frequently there, Prof.

1) KJERULF „Sparagmittfeldet". Universitetsprogram Kristiania. 1872. p. 81. Fig. 7—9.

2) BRÖGGER, Om Paradoxidesskifrene ved Krekling. Nyt Magazin for Naturvidenskab. 1878. Bd. 24. p. 58.

3) LINNARSSON, De undre Paradoxideslagren vid Andrarum. Sveriges geologiska Undersökning 1882. Ser. C. N^o. 54. p. 21. Taf. IV. fig. 3, 4.

MOBERG supposing that my Trilobites-remains would prove to belong to this species, which is not always to be distinguished from Arionellus Primaevus.

Indeed, I had been thinking of this species, but as LINNARSSON declares that here the vaulted part of the mid-shell before the glabella towards the outside slopes strongly down, I thought I could not range my remains under this head. The mid-shell I received from Lund confirmed my opinion. I informed Prof. MOBERG of this and sent him a few plaster-casts of the Trilobites-remains occurring in the erratic-block found at Vries. I was answered that Prof. MOBERG shared my opinion and considered them as having come from Arionellus Primaevus. At the same time he was so kind as to send me a plaster-cast of the best of the mid-shells of this species of Trilobites, found in the collection at Lund. Now I could ascertain that in Arionellus Primaevus the part of the cephalon in front of the glabella does not turn down, which is not specially mentioned by BRÖGGER and LINNARSSON.

Also in the mid-shell of which MOBERG sent me a plaster-cast, the breadth of the glabella diminishes but little towards the front, though its length is about 14 millimetres.

I think, then, that we now may with certainty conclude, that in the Vries erratic-block we find remains of Arionellus Primaevus BRÖGGER. As this Trilobite occurs only in layers that contain remains of Holmia (Olenellus) Kjerulfi LIXRS, and as these are taken to be the youngest of the Under-Cambrian ones, the age of the layer of which this erratic-block in former times formed part, may be easily determined.

Besides occurring at Tömten in Norway and at Forsemölla near Andrarum in Schonen, which places I mentioned already, Arionellus Primaevus is probably found in two more places in firm rock, viz. at Kiviks Esperöd to the North and at Gislöfs Hammar to the South of Simrishamn in Schonen. The former place was first made mention of by NATHORST¹⁾, who told that he had found there an off-print of an Arionellus? That in Gislöfs Hammar remains of an Arionellus occur, was first communicated to us by LINNARSSON, in his description of the Arionellus-remains of Forsemölla. According to this writer, many of the mid-shells found there by VON SCHMALENSSEE much resembled the larger shells of Forsemölla, which he dared not with certainty call Arionellus Primaevus.

¹⁾ NATHORST. Om de kambriska och siluriska lagren vid Kiviks Esperöd etc. Geol. Föreningens i Stockholm Förhandlingar. Bd. 3. 1877. p. 264.

As for two kinds occurring in the same place, HOLST ¹⁾ mentions that the "gråvackeskiffer" may also contain a species of *Arionellus* (*Arionellus Primaevus* BRÖGGER ²⁾).

From communications made by TULLBERG ³⁾ and HENNIG ³⁾ the conclusion might be drawn that *Arionellus Primaevus* BRÖGG occurring at Kiviks Esperöd and Gislöfs Hammar, had been sufficiently indicated. I think, however, that this should not be done. The list of fossils which these two authors have drawn up with regard to the "gråvackeskiffer" of the two places mentioned just now and of Andrarum, must refer, in my opinion, to these places taken collectively and not to each separately. I am confirmed in this opinion by the fact that remains of *Holmia Kjerulfi* LINNÉ (or of a kindred species) are not mentioned by MOBERG ⁴⁾ as being found at Kiviks Esperöd, whereas they are mentioned by them.

The origin of this erratic-block must most probably be looked for in the eastern part of Schonen or in the Baltic Sea-region bordering on it. That petrographically it differs from the ordinary "gråvackeskiffer", does not clash with this opinion, several writers informing us that the latter often changes into sandstone. The thin layers on the lower side indicate that something of the kind has been the case here.

It is not likely to have come from Norway, for never was a sedimentary erratic-block found in these parts, of which this may be said.

As was mentioned above, I take this erratic-block to be the most interesting one of the pieces that are described in this paper. I do this because it is the first piece coming from layers with *Holmia Kjerulfi* LINNÉ that has ever been made mention of. Nowhere in literature did I find anything about an erratic-block of that age.

IV. Shortly before the summer-holidays of last year I found, when visiting the loam-pit close by Hemelum, a slab-shaped piece of fine-grained sandstone three centimetres thick, whilst its largest dimension is a little more than 20 centimetres. It is layered and contains calcium-carbonate, so that with muriatic acid it gives effervescence of dioxide-carbonate.

Owing to the large number of Glauconite-grains it contains, the

¹⁾ HOLST. Beskrifning till kartbladet Simrishamn, p. 17.

²⁾ TULLBERG, Skånes Graptoliter. I. Allmän öfversigt öfver de siluriska bildingarne i Skåne och jemförelse med öfriga kända samtida afslagningar. Sveriges geologiska Undersökning. 1882. Ser. C No. 50. p. 26.

³⁾ HENNIG, Geologischer Führer durch Schonen. 1900. p. 26.

⁴⁾ MOBERG, Sveriges äldsta kända Trilobiter.

stone of which this erratic-block consists is coloured a strong green. This is the case with some layers especially. Some particles of a light-coloured kind of glimmer are found in it.

My attention was drawn to this kind of sandstone, because, when splitting this erratic-block into two parts, I found that it contains Hyolithus-remains, viz. grey-coloured stone-kernels. The lower part of one of them is brown.

When visiting the Natural History-Museum at Hamburg last summer, and admiring its collection of sedimentary erratic-blocks, I asked Prof. GOTTSCHÉ whether he knew of suchlike erratics. Prof. GOTTSCHÉ thought he remembered such pieces to have been found in the surroundings of Hamburg. Owing to want of exposing-room, however, they lay packed up among other pieces, in consequence of which they could not be shown me. He drew my attention to the fact that in this kind of erratic-blocks sometimes occur small conical valves of horn-shelled Brachiopodes. These valves were shown to me in a brown-coloured erratic-block.

A short time after I found on the beach at Borgholm in Oeland not only an erratic-block with Hyolithus-rests entirely corresponding with my Hemelum piece, but also a brown piece of sandstone with a valve of a small horn-shelled Brachiopode.

I searched my books for anything on the subject of this kind of erratics or stone, but at first without any result.

As Prof. MOBERG at Lund in the summer of 1901, when I had requested him to be so kind as to give me some information concerning Oeland, had noted down on my map of this island that on its coast, to the North of Färjestaden, occur erratic-blocks with *Discinella Holsti* (then unknown to me), and the valves of Brachiopodes I had found were, like those of *Discina*, horny and flat-conical, but much smaller, I supposed that Prof. MOBERG could give me some information about this stone. For this reason I intended to write to him concerning this subject, and, was going to do so, when accidentally I discovered in the essay of HOLM¹⁾ on the Swedish Hyolithidae and Conulariidae, that by MOBERG²⁾ a greenish kind of sandstone, rich in Glauconites, with *Discinella Holsti* MOBERG and Hyolithes, occurring as erratic-blocks in Oeland, had been described.

Having studied MOBERG's essay, I find that the stone of which my

¹⁾ HOLM. SVERIGES Kambrisk-Siluriska Hyolithidae och Conulariidae. SVERIGES Geologiska Undersökning. Ser. C. No. 112.

²⁾ MOBERG. Om en nyupptäckt fauna i block of kambrisk sandsten, insamlade of dr. N. O. HOLST. Geologiska Föreningens i Stockholm Förhandlingar 1902. No. 142. Bd. 14. Häft 2. p. 103.

erratic-blocks with Hyolithus-remains consist, has been described by this author as type *a*. The piece of brown sandstone with the valve of a small Brachiopode I found at Borgholm, belongs to his type *d*. The fossil occurring in it has been determined by me as a vaulted valve of *Discinella Holsti* MOBERG. The erratic-block that was shown me by GOTTSCHÉ probably belongs to the same type; the organic remains occurring in it are likely to have come from the same species of Brachiopodes.

The Hyolithus-remains in the Hemelum erratic-block have been very imperfectly preserved, which, according to HOLM,¹⁾ is usually the case with this stone. A longitudinal section possesses a length of 10 millimetres and at the mouth a breadth of 4 millimetres, so the dimensions of this shell remind of the one pictured and described by MOBERG²⁾ under the name of *Hyolithus Insularis* nov. spec., whereas HOLM afterward called it *Hyolithus Confusus* nov. spec.

The relative age of this kind of erratic-blocks does not seem to be with certainty known yet, as up to this time no corresponding stone has been met with as firm rock, and the organic remains found in them have not yet been discovered in company with such as might contribute to the solution of this question. MOBERG, however, thinks he may conclude from the general character of the fossils occurring in them, from their petrographical nature and from the way in which they are spread, that they come from Under-Cambrian layers.

HOLST³⁾ draws the same conclusion, after tracing the manner in which they are spread. I think I may infer from his essay, that in his opinion they come from the youngest Under-Cambrian layers. In accordance with this is the presence of *Discinella*-remains, this genus of Brachiopodes occurring, according to MOBERG, in North-America, in layers containing *Olenellus*.

As was said just now, a corresponding kind of stone was not yet met with as firm rock. Most probably it formerly occurred westward of Oeland; it may be found there even now at the bottom of the sea, because this kind of erratic-blocks is found in large numbers only on the western coast of this island, between Halltorp and Mörbylånga, and on the little isles and cliffs in the neighbourhood. Less numerous they are in the other parts of the eastern and western coasts of the Kalmarsund.

1) HOLM loc. cit. p. 74.

2) MOBERG. Om en nyupptäckt fauna i block of kambrisk sandsten etc. p. 117.

3) HOLST. Bidrag till kännedomen om lagerföljden inom den kambriska sandstenen, p. 9.

MOBERG says that these erratics were found by Dr. HOLST on Bornholm, too. Neither in German nor in Dutch literature have I been able to find anything concerning suchlike erratic-blocks. It is almost doubtless, however, that they are mentioned by GOTTSCHÉ¹⁾ as "Cambrische Grauwackeschiefer". Only those erratic-blocks which, according to him, resemble the Swedish "Grävackeskifer", must be taken into consideration then. The description of the latter entirely corresponds with that of type *a* by MOBERG. The small, round, horny-lustrous Brachiopodes-valves with a diameter of 2 millimetres, mentioned by GOTTSCHÉ, which may come from *Discinella Holsti* MOBERG, also cause us to conclude that we have the same kind of stone here. GOTTSCHÉ does not inform us of Hyolithus-remains occurring in suchlike erratic-blocks. No erratics containing them had perhaps been found at the time. It follows from what he orally communicated to me, that now they have most probably been found.

The same author says that according to LINNARSSON a kind of stone entirely corresponding with the one described by him, has been met with by HUMMEL near Tereskov (wich HUMMEL calls Torekov), on the coast of N. W.-Schonen, as firm rock. Judging from the description HUMMEL²⁾ gives of it, it much resembles, petrographically, type *a* of the *Discinella Holsti*-sandstone. HUMMEL does not say, however, that fossils are found in it. Perhaps we have here the same case as with the Glauconitic sandstone from the neighbourhood of Simrishamn, of which HOLST³⁾ writes that a corresponding kind frequently occurs in the "sandstone-region" of the Kalmarsund. Here, too, the resemblance seems to be petrographic at best, for MOBERG, in his essay, speaks about this sandstone no more than about that of TOREKOV.

Most probably the thin-layered, greenish stone which resembles the "Grauwacken-Schiefer" of the *Olenellus Kjerulfi*-region, and which petrographically keeps the medium between the *Olenellus*-stone of Hardeberga in Schonen and the equally old "grön skiffer" of Bornholm, with stone-kernels of a Brachiopode probably belonging to *Acrothele*, and with Hyolithus-remains bearing the greatest resemblance to *Hyolithus Lenticularis* Holm, as STOLLEY⁴⁾ writes, — is also *Discinella Holsti*-sandstone.

¹⁾ GOTTSCHÉ. Die Sedimentär-Geschiebe der Provinz Schleswig-Holstein. 1883. p. 8.

²⁾ HUMMEL. Beskrifning till kartbladet „Båstad". (No. 60). SVERIGES geologiska Undersökning. 1877. p. 10.

³⁾ HOLST. Beskrifning till kartbladet Simrishamn. p. 15.

⁴⁾ STOLLEY. Die cambrischen und silurischen Geschiebe Schleswig-Holsteins. Archiv für Anthropologie und Geologie Schleswig-Holsteins und der benachbarten Gebiete. 1895. Bd. I. Heft. 1. p. 130.

Finally I must mention that, on the occasion of a later visit to the loam-pit near Hemelum, I found two more erratic-blocks, which must probably also be counted among pieces of *Discinella* Holstisandstone. Neither contains any fossils. One corresponds petrographically with what was described; the other is for the greater part white, but possesses green layers. If I am not mistaken, I sometimes saw suchlike stones on the beach of Borgholm.

Physics. — “*On the course of the values of b for hydrogen, in connection with a recent formula of Prof. VAN DER WAALS.*”
By Dr. J. J. VAN LAAR. (Communicated by Prof. J. D. VAN DER WAALS).

1. Making use of the theory of *cyclic* motions, Prof. VAN DER WAALS has given a new deduction of the equation of state of a simple substance, in which the size of the molecule appeared to be variable, and to be a function of the *volume*¹⁾.

For a bi-atomic gas the following formula has been found:

$$\frac{b-b_0}{v-b} = 1 - \left(\frac{b-b_0}{b_g-b_0} \right)^2 \dots \dots \dots (1)$$

Here b_0 denotes the smallest value of b , corresponding to the case that the two atoms of a molecule touch each other; b_g represents the greatest value i. e. the value for very great (infinitely great) volume. The above equation may be easily derived from the so called “equation of state of the molecule”:

$$\left[p + \frac{a}{v^2} + \alpha(b-b_0) \right] (b-b_0) = RT, \dots \dots \dots (a)$$

when we take $v = \infty$, in which case b assumes the value b_g and $p + \frac{a}{v^2}$ may be neglected with respect to $\alpha(b-b_0)$. So we get:

$$\alpha(b_g-b_0)^2 = RT.$$

If we substitute this value into equation (a), paying regard to

$$p + \frac{a}{v^2} = \frac{RT}{v-b},$$

we get the equation

$$\left(\frac{1}{v-b} + \frac{b-b_0}{(b_g-b_0)^2} \right) (b-b_0) = 1,$$

which yields immediately equation (1).

¹⁾ These Proceedings of the meetings of February, March and April 1901. See also “*Livre jubilaire dédié à J. BOSSCHA*” of the *Arch. Néerl.*, p. 47. (The first communication and part of the second discuss principally the specific heat for very large volume).

The quantity a in the equation of state (a) depends on the forces, which keep the atoms together in the molecule. These forces are supposed to be proportional to the linear deviation from the position of equilibrium $v - v_0$.

The equation of state (a) for a tri-atomic gas, e. g. CO_2 — which in this case is the combination of two similar equations — will contain besides RT still a factor f , whose value will vary from 1 to 2 according as the different cases occur, which we may distinguish in the motion of the atoms. For CO_2 a value of nearly 2 is found for f . As, however, this quantity f for a certain substance is, strictly speaking, variable (see the paper in the “*Livre dédié à BOSSCHA*”, quoted above) and as the accurate equation is therefore very complicate, I have chosen a bi-atomic gas, namely hydrogen, in order to test the new equation of VAN DER WAALS. In this case $f = 1$ and the relation between b and v is represented by the simple equation (1). I hope later to test the equations for oxygen and nitrogen, in order to examine whether the results found for hydrogen also hold for these gases.

II. An *accurate* knowledge of a is required for the exact calculation of b . This is still a great difficulty. *Absolute* certainty as to this value cannot be obtained as yet, but still it appears to me that the value $a = 300 \times 10^{-6}$ ¹⁾ has a high degree of probability. Assuming another value for a , I found namely that the values calculated for b decrease much too rapidly, — much more rapidly than agrees with formula (1); this is principally the case in the beginning, i. e. for large values of v . Only the values of b , calculated for $a = 300 \times 10^{-6}$ varied in such a way, that their course was represented by equation (1) with nearly perfect accuracy. SCHALKWIJK ²⁾ also calculated from his last experiments $10^6 a = 300$ ($10^6 b_g = 910$). I therefore thought myself justified in assuming 300 for $10^6 a$. In the following table we find the values for b at 0° Centigrade, calculated from the equation

$$\left(p + \frac{a}{v^2}\right)(v-b) = (1+a)(1-b)(1+av).$$

For $(1+a)(1-b)$ we put 0,9994. All values have been multiplied by 10^6 ; the same will be the case with all values of b which we give in what follows.

At 0° C. we have:

$$v-b = \frac{0,9994}{p + \frac{a}{v^2}}.$$

¹⁾ All values of v , b , etc. have been expressed in the usual practical units.

²⁾ These Proceedings, June 1901, p. 124.

0° C.

p	$v^1)$	v^2	$\frac{a}{v^2}$	$r-b$	b found.	b calculated from (1)	Δ
100	10690	114.3	2.6 ²	9739	951	907	+44
150	7353	54.07	5.5 ⁵	6425	928	901	+27
200	5690	32.38	9.2 ⁶	4777	913	896	+17
250	4692	22.01	13.6 ³	3791	901	891	+10
300	4030	16.24	18.4 ⁷	3138	892	886	+6
350	3560	12.67	23.6 ⁸	2675	885	880	+5
400	3207	10.28	29.1 ⁸	2329	878	875	+3
450	2933	8.602	34.8 ⁷	2061	872	870	+2
500	2713	7.360	40.8	1848	865	865	± 0
550	2533	6.416	46.8	1675	858	860	-2
600	2386 ⁵	5.695	52.7	1531	855	855	± 0
650	2259	5.103	58.8	1410	849	850	-1
700	2149 ⁵	4.620	64.9	1307	843	845	-2
750	2053	4.215	71.2	1217	836	840	-4
800	1971	3.885	77.2	1139	832	835	-3
850	1897	3.599	83.4	1071	826	830	-4
900	1833 ⁵	3.362	89.2	1010	823	826	-3
950	1774	3.147	95.3	956	818	821	-3
1000	1722 ⁵	2.967	101.1	908	815	817	-2
1100	1637	2.680	111.9	825	812	809	+3
1200	1557 ⁵	2.426	123.7	757	801	801	± 0
1300	1491	2.223	135.0	696	795	793	+2
1400	1432	2.051	146.3	646	786	785	+1
1500	1380	1.904	156.3	603	777	777	± 0
1600	1334 ⁵	1.781	168.4	565	769	770	-1
1700	1294 ⁵	1.681	178.5	532	762	763	-1
1800	1258	1.583	189.5	502	756	756	± 0
1900	1225	1.501	199.9	476	749	749	± 0
2000	1194 ⁵	1.427	210.2	452	742	743	-1
2100	1166 ⁵	1.361	220.4	431	736	736	± 0
2200	1141	1.302	230.4	411	730	730	± 0
2300	1118	1.250	240.0	393	725	724	+1
2400	1097 ⁵	1.205	249.0	377	720	719	+1
2500	1078	1.162	258.2	362	716	714	+2
2600	1059 ⁵	1.123	267.1	349	711	710	+1
2700	1042	1.086	276.2	336	706	705	+1
2800	1024 ⁵	1.050	285.7	324	701	700	+1

¹⁾ Up to 1000 atmospheres the values of r have been borrowed from the results of the "second method" of AMAGAT (méthode des regards); from 600 atm. to

The values of v have been borrowed from the well known experiments of AMAGAT ¹).

The too large values of b in the beginning — here only to about 300 atm. — are still present. This indicates probably that the value $a = 300$ is still slightly too great. But from 300 atm. upwards the agreement is quite satisfactory. Small inaccuracies in the determination of the value of v have for large volumes a great influence on the values of b . To this circumstance also it may be ascribed that the values of b are in the beginning not reliable. So the value $v = 10690$ at $p = 100$ cannot be accurate to a higher degree than to ten units at the utmost. So it might also have been 10680 or 10670 and b or $v - (v - b)$ might have been 10 or 20 units smaller. The values of b "calculated" have been determined with the aid of equation (1) in the assumption

$$\underline{b_g = 917} \quad ; \quad \underline{b_0 = 463}.$$

b_0 may be determined in the following way. If we substitute into (1)

$$\frac{b - b_0}{b_g - b_0} = x,$$

and pay regard to $b - b_0 = \frac{x}{1-x} (b_g - b)$, then we get for (1):

$$\frac{x}{1-x} \frac{b_g - b}{v - b} = 1 - x^2,$$

and therefore:

$$\frac{b_g - b}{v - b} = \frac{1-x}{x} (1-x^2).$$

For an assumed value of b_g this equation enables us to determine the corresponding value of x from v and b at e.g. 500, 1000, 1600, 2200, 2800 atm. The value of b_0 may then be calculated from

$$b_0 = b - (1 - x^2) (v - b),$$

which follows immediately from (1). So I found with $b_g = 917$ at 1000, 1600, 2200, 2800 atm. respectively the values $b_0 = 455, 463, 462, 466$. If we put $a = 400$ instead of $a = 300$, then we find with $b_g = 1000$ at $p = 2800$ atm. in the same way $b_0 = 463$. With

1000 atm. the values of v at 600, 700, 800, 900 and 1000 atm. represent the mean values of the results of the first method (that of the electrical contacts) and those of the second method. From 1100 atm. upwards the values of v have been determined by the first method.

¹) Mémoires sur l'élasticité et la dilatabilité des fluides jusqu'aux très hautes pressions, p. 32—33 and 38.

$a = 500$, $b_g = 1100$ we find at 2800 atm. again $b_0 = 464$. So we may assume with perfect certainty b_0 to differ very little from 463.

With this value of b_0 in the first place b_g was again calculated. From (1) follows:

$$\frac{(b-b_0)^2}{(b_g-b_0)^2} = 1 - \frac{b-b_0}{v-b} = \frac{(v-b) - (b-b_0)}{v-b},$$

so

$$b_g - b_0 = (b - b_0) \sqrt{\frac{v-b}{(v-b) - (b-b_0)}}.$$

In this way I found at $p = 500, 600, 700, 800, 900, 1000, 1200, 1400, 1600, 1800, 2000$ atm. respectively $b_g = 918, 917, 914, 912, 912, 913, 919, 917, 917, 917, 917$. From these values I concluded that $b_g = 917$.

After that the values of b (calculated) were determined as follows. We derive from equation (1):

$$\frac{b-b_0}{(v-b_0) - (b-b_0)} = 1 - \frac{(b-b_0)^2}{(b_g-b_0)^2}.$$

If we put $b-b_0 = y$, then we get for $b_g-b_0 = 454$:

$$\frac{y}{(v-b_0) - y} = 1 - \frac{y^2}{454^2},$$

from which follows:

$$y = 454 \sqrt{\frac{(v-b_0) - 2y}{(v-b_0) - y}}.$$

We know the values of y already in approximation from b (found). These values, substituted into the second member of the above equation, yield the accurate value of y , and so also of b .

III. Let us begin with assuming that the values of b_0 and b_g are independent of the temperature, which follows from the supposition of Prof. VAN DER WAALS, that the quantity α , which depends on the forces between the atoms, is proportional to the absolute temperature. Then we may calculate the *critical* quantities in the following way. Equation (1) in connection with the following equation:

$$v_k = \frac{3b_k}{1 + 2(\beta_1 + \beta_2)} \text{ or } v_k - b_k = \frac{2}{3} v_k (1 - \beta_1 - \beta_2),$$

where

$$\beta_1 = \left(\frac{db}{dr} \right)_k; \quad \beta_2 = - \frac{1}{2} (v_k - b_k) \cdot \frac{\left(\frac{d^2b}{dr^2} \right)_k}{1 - \left(\frac{db}{dr} \right)_k}.$$

yields after some reductions ¹⁾:

$$\frac{3}{2} \frac{1}{1+(1-x)\left(1+\frac{\mu}{\sqrt{x}}\right)} = \frac{1+\left(\frac{1-x}{1+x}\right)^3}{\left(1+\frac{(1-x)^2}{1+x}\right)^2}.$$

Here is $x = \left(\frac{b-b_0}{b_g-b_0}\right)^2$ and $\mu = \frac{b_0}{b_g-b_0}$. We may write for the second member:

$$\frac{2(1+3x^2)}{(1+x)(2-x+x^2)^2}$$

Therefore we get also:

$$2-x+\mu \frac{1-x}{\sqrt{x}} = \frac{3(1+x)(2-x+x^2)^2}{1+3x^2}. \quad \dots \quad (b)$$

The value of x may be derived from this equation. As $b_g=917=1,98b_0$, μ gets the value $\frac{1}{0,98}=1,02$, and we find in approximation for x the value 0,709.

Therefore

$$\frac{b_k-b_0}{b_g-b_0} = \sqrt{0,709} = 0,842,$$

from which we may easily derive:

$$\underline{b_k = 0,922 b_g = 845.}$$

Now we have:

$$\frac{3}{2} \frac{v_k-b_k}{v_k} = 1-\beta_1-\beta_2 = \frac{2(1+3x^2)}{(1+x)(2-x+x^2)^2} = 0,9163,$$

from which we find:

$$v_k = 2,57 b_k; \quad \beta_1 + \beta_2 = 0,0837.$$

The critical volume is therefore:

$$\underline{v_k = 2,57 b_k (= 2,37 b_g = 4,69 b_0) = 2172.}$$

At 0° C. this volume is (comp. the table) already reached at a pressure of about 700 atm. The values of v at 0° range in the experiments of AMAGAT to 1025; the verification of equation (1) of VAN DER WAALS may therefore be extended over volumes which have the size of liquid volumes; this fact compensates the want of experiments below the critical temperature.

We may also calculate the quantities β_1 and β_2 separately. From ²⁾

¹⁾ See v. D. WAALS, l. c. III, p. 652.

²⁾ VAN DER WAALS, l.c. III, p. 651.

$$\beta_1 = \frac{1}{1 + \frac{1}{(1-x)^2}} = \frac{(1-x)^2}{2-x+x^2}$$

follows :

$$\underline{\beta_1 = 0,0472} ; \quad \underline{\beta_2 = 0,0365}.$$

We find for $T_k T_k$:¹⁾

$$RT_k = \frac{8}{27} \frac{a}{b_k} \frac{(1-\beta_1-\beta_2)^2(1+2(\beta_1+\beta_2))}{1-\beta_1}$$

or

$$RT_k = \frac{8}{27} \frac{a}{b_k} \times \frac{0,8396 \times 1,1674}{0,9528} = 1,029 \times \frac{8}{27} \frac{a}{b_k} = 0,305 \frac{a}{b_k}.$$

With $a = 300$, $b_k = 845$ we find therefore:

$$RT_k = 0,9994 \frac{T_k}{273} = 0,108,$$

which gives:

$$\underline{T_k = 29^\circ,5},$$

DEWAR found $T_k = 30^\circ$ à 32° 2).

The critical pressure is represented by 3)

$$p_k = \frac{1}{27} \frac{a}{b_k^2} \frac{(1-\beta_1-4\beta_2)(1+2(\beta_1+\beta_2))^2}{1-\beta_1},$$

or

$$p_k = \frac{1}{27} \frac{a}{b_k^2} \times \frac{0,8068 \times 1,363}{0,9528} = 1,154 \times \frac{1}{27} \frac{a}{b_k^2} = 0,0427 \frac{a}{b_k^2}.$$

Introducing into this expression the values of a and b_k , we find:

$$\underline{p_k = 18,0 \text{ atm.}}$$

DEWAR found 15,4 atm.; OLZEWSKI 4) 20 atm.

We find for the so called critical coefficient X :⁵⁾

$$X = \left(\frac{pv}{RT} \right)_k = \frac{3}{8} \times \frac{1-\beta_1-4\beta_2}{(1-\beta_1-\beta_2)^2}.$$

or

$$X = \frac{3}{8} \times \frac{0,8068}{0,8396} = \frac{3}{8} \times 0,961 = \underline{0,360}.$$

Finally the quantity \mathcal{N} may be calculated from 6)

1) Id. II, p. 583.

2) Proc. Royal Inst. 16 (2), N^o. 94 (1901), p. 477.

3) v. D. WAALS, l. c. II, p. 583.

4) Wied. Ann., 56, p. 133 (1895). See also VERSCHAFFELT, These Proceedings, Febr., 1899, p. 327.

5) v. D. WAALS, l. c. II, p. 584.

6) Id. III, p. 648.

$$Y = \left(\frac{T}{p} \frac{dp}{dT} \right)_k = 4 \frac{1 - \beta_1 - \beta_2}{1 - \beta_1 - 4\beta_2} = 4 \times \frac{0,9163}{0,8068} = 4 \times 1,136 = \underline{4,545}.$$

Just as X comes again very close to the normal value 0,375, so Y for hydrogen approaches again close to the theoretical value 4. The expressions for T_k and p_k differ only little from those, found for these quantities for tri-atomic gases, such as CO_2 ; the expression for v_k on the other hand deviates strongly from it. This is to be ascribed to the fact, that b_g has here not the value of nearly four-times b_0 , but amounts to only twice that value. The quantities β_1 and β_2 are therefore much smaller than in the case of tri-atomic gases.

VAN DER WAALS found for CO_2 e.g. $\beta_1 = 0,138$ and $\beta_2 = 0,1$, the values we found above amounting to only about one third of these values. b_k is also in this case not $0,86 b_g$ but $0,92 b_g$, and for v_k we find $2,57 b_k$ instead of $2,03 b_k$, or $2,37 b_g$ instead of $1,75 b_g$.

It is certainly of the highest importance to know whether the result for v_k agrees with the experiments. At the same time the value of the critical coefficient X will then agree, for the values of T_k and p_k agree very well. But with the investigation of this question, and with the verification of Y , we will wait till we have investigated the behaviour of b at higher temperature, which will be done in the next chapter.

IV. In the first place we will repeat the calculations of § 2 at $99^{\circ},25$ C. We derive the following table (p. 581) from the experiments of AMAGAT¹⁾ at that temperature.

$v-b$ has here been calculated from

$$v-b = \frac{0,9994 (1 + 99,25 \times 0,0036627)}{p + \frac{a}{r^2}} = \frac{1,3627}{p + \frac{a}{r^2}}.$$

For the "calculated" values of b I determined quite in the same way as is indicated above for 0° :

$$\underline{b_g = 917} \quad ; \quad \underline{b_0 = 386}.$$

Again the initial values of b "found" (up to about 400 atm.) are too great. But afterwards the agreement is sufficient, though the verification was only possible up to 1000 atm., as, alas, no further experiments were available. We come to the remarkable result, that the value of b_0 has considerably decreased though the limiting value of b has remained unchanged. It seems that at higher temperature the atoms in the molecule may approach one another closer than at lower temperature.

¹⁾ l. c. p. 38 (2nd method).

p	r	v^2	$\frac{a}{v^2}$	$r-b$	b found	b calculated from (1)	Δ
150	9846	96.94	3.0 ⁹	8902	944	902	+42
200	7567	57.26	5.2 ⁴	6640	927	897	+30
250	6200	38.44	7.8 ⁰	5286	914	892	+22
300	5286	27.94	10.7 ⁴	4385	901	887	+14
350	4636	21.49	13.9 ⁶	3744	892	881	+11
400	4147	17.20	17.4 ⁴	3265	882	876	+ 6
450	3766	14.48	21.1 ⁶	2892	874	871	+ 3
500	3462	11.99	25.0 ²	2596	866	866	± 0
550	3214	10.33	29.0 ⁴	2353	861	861	± 0
600	3006	9.036	33.2 ⁰	2152	854	856	- 2
650	2831	8.015	37.0	1983	848	851	- 3
700	2680	7.182	41.8	1837	843	846	- 3
750	2551	6.508	46.1	1712	839	841	- 2
800	2436	5.934	50.6	1602	834	836	- 2
850	2336	5.457	55.0	1506	830	831	- 1
900	2244	5.036	59.6	1420	824	827	- 3
950	(2174)	4.726	63.5	1345	(829) ¹⁾	822	-
1000	2093	4.381	68.5	1275	818	818	± 0

From equation (a) follows that for great volumes:

$$a(b_g - b_0)^2 = RT.$$

Now we find:

$$0^\circ \quad | \quad b_g - b_0 = 454 \quad | \quad (b_g - b_0)^2 = 20,61 \times 10^4$$

$$100^\circ \quad | \quad ,, = 531 \quad | \quad = 28,20 \quad ,,$$

$(b_g - b_0)^2$ has therefore increased in the ratio 1 : 1,368. But T has increased in the ratio 1 : 1,364, from which would follow that a is independent of T .

In order to investigate whether this also applies to still higher temperatures, I have also performed the calculation for 200°,25.

$r-b$ may then be calculated from:

$$r-b = \frac{0,9994(1+200,25 \times 0,0036627)}{p + \frac{a}{r^2}} = \frac{1,7324}{p + \frac{a}{r^2}}$$

¹⁾ The value given for r at $p=950$ atm. appears to be erroneous; probably it must be 2164.

With the aid of the following table we may survey the results.
200° C.

p	v	r^2	$\frac{a}{v^2}$	$v-b$	b		Δ
					found	calculated	
150	12320	451.78	4.98	41399	921	894	+27
200	9420	88.74	3.38	8518	902	889	+13
250	7680	58.98	5.09	6791	889	884	+ 5
300	6520	42.51	7.06	5642	878	879	- 1
350	5694	32.42	9.25	4822	872	873	- 1
400	5075	25.76	11.65	4208	867	868	- 1
450	4593	21.10	14.22	3732	861	863	- 2
500	4210	17.72	16.93	3351	859	858	+ 1
550	3891	15.14	19.82	3040	851	853	- 2
600	3627	13.16	22.80	2782	845	848	- 3
650	3403	11.58	25.91	2563	840	843	- 3
700	3211	10.31	29.10	2376	835	838	- 3
750	3045	9.272	32.46	2214	831	833	- 2
800	2900	8.410	35.67	2073	827	828	- 1
850	2772	7.684	39.0	1949	823	823	\pm 0
900	2657	7.060	42.5	1838	819	819	\pm 0

Only at 150 and 200 atm. the values for b "found" are somewhat too high; further on the agreement is satisfactory. The experiments ranged only to 900 atm. The values of b "calculated" have been determined from (1) with the aid of:

$$\underline{b_g = 910}; \quad \underline{b_0 = 306}.$$

b_g appears to be slightly smaller than at 0° and 100°, but b_0 has again strongly decreased. It is a remarkable fact that the decrease of b_0 between 0° and 99° amounts to 77, and that between 99° and 200° to 80; so for each degree the same amount namely 0,8.

As to $b_g - b_0$; we have now:

$$0^\circ \quad b_g - b_0 = 454 \quad | \quad (b_g - b_0)^2 = 20,61$$

$$200^\circ \quad \dots = 604 \quad | \quad \dots = 36,48$$

The ratio of the values of $(b_g - b_0)^2$ is 1,77. For 1+ at we find 1,73. Taking for $b_g - b_0$ at 200° a value which is only 6 units

smaller, namely 598, the ratio of the values of $(b_g - b_0)^2$ would also have been found equal to 1,73. We may therefore safely assume that $(b_g - b)^2$ is found to be accurately *proportional* to the temperature within so large an interval of temperature as that between 0° and 200° , in consequence of which the quantity a must be *quite independent* of the temperature.

It is not astonishing that a is independent of the temperature; the contrary would rather seem to be remarkable. Being induced to make this contrary supposition for the better agreement of the quantity $\frac{T}{p} \left(\frac{dp}{dT} \right)_k$ for CO_2 with the experiments, Prof. v. D. WAALS¹⁾ immediately pointed out its astonishing character.

We shall just draw attention to the following consequence of the fact, that $b_g - b_0$ is proportional to \sqrt{T} .

If we put:

$$b_g - b_0 = \sqrt{\gamma T},$$

then equation (1) may be written as follows:

$$\frac{b - b_g + \sqrt{\gamma T}}{c - b} = 1 - \frac{(b - b_g + \sqrt{\gamma T})^2}{\gamma T} = 2 \frac{b_g - b}{\sqrt{\gamma T}} - \frac{(b_g - b)^2}{\gamma T}.$$

With small value of $b_g - b$ and great value of v , we get approximately:

$$\frac{\sqrt{\gamma T}}{v} = 2 \frac{b_g - b}{\sqrt{\gamma T}},$$

therefore

$$b_g - b = \frac{\gamma T}{2v}.$$

v being in this case approximately equal to $\frac{RT}{p}$, we get:

$$b_g - b = \frac{\gamma}{2R} \cdot p,$$

or

$$\underline{b = b_g - \gamma' p},$$

i.e. the value of b depends only on p and no more on r or T , the value of b_g being nearly constant. The values of b , calculated for *the same* pressures, have therefore the same difference whether the temperature be 0° or 200° . For we have:

$$b_1 - b_2 = \gamma' (p_2 - p_1).$$

We found this fact affirmed in the above tables²⁾. For the purpose

¹⁾ l. c. III, p. 646.

²⁾ I pointed this out already before in a paper in the *Archives Teyler* („Sur l'influence des corrections, etc.” (2) VII, 3me partie, p. 26—27.) I tested there the b -values for hydrogen to an empirical formula of KAMERLINGH ONNES.

of a more direct comparison we collect the values of b for pressures differing each time 100 atm. in another table.

p	b		
	0°	100°	200°
100	907	—	—
	41		
200	896	897	889
	10	10	10
300	886	887	879
	11	11	11
400	875	876	868
	10	10	10
500	865	866	858
	10	10	10
600	855	856	848
	10	10	10
700	845	846	838
	10	10	10
800	835	836	828
	9	9	9
900	826	827	819
	9	9	
1000	817	818	—

We see that the differences are the same. All the values of b at 200° are 8 units less than the corresponding values at 0° and at 100°, because the value of b_g at 200° is 7 units less. But the course is always just the same. And as at a given value of p we always find *increasing* values of v at increasing temperature, so the value of b_0 must of course always decrease.

From the above follows also, that we may determine b_g immediately, e.g. adding 52 units to the values of b found at 500 atm., or 32 units to that at 400 atm., etc.

On the preceding reasoning we may base the following short calculation.

At $p_2 - p_1 = 100$ the initial value of $b_1 - b_2$ amounts to circa 10 à 11; we have therefore:

$$\gamma' = \frac{\gamma}{2R} = \frac{10,5 \times 10^{-6}}{100} = 0,105 \times 10^{-6}.$$

Therefore

$$b_g - b_0 = \sqrt{\gamma T} = 10^{-3} \sqrt{0,21 RT} = 10^{-3} \sqrt{0,21 \times 0,9994 (1 + at)},$$

or

$$b_g - b_0 = 10^{-6} \sqrt{21 \times 10^4 (1 + at)}.$$

So we have at 0° $10^6(b_g - b_0) = 458$ (found 454).

At 100° we find $10^6(b_g - b_0) = \sqrt{21 \times 10^4 \times 1,3627} = 535$ (found 531).

At 200° we find $10^6(b_g - b_0) = \sqrt{21 \times 10^4 \times 1,7324} = 603$ (found 604).

V. A slight correction must of course be applied to the calculations of § 3 in consequence of the variability of $b_g - b_0$ with the temperature. For the assumption that b_g remains constant pleads also the circumstance, that according to an observation of D. BERTHELOT the experiment yields the value 2,93 à 2,98 for the ratio between the temperature at which a gas in extreme rarefaction follows the law of BOYLE, and the critical temperature; for which ratio the supposition that b_g is constant over this large temperature interval ¹⁾ leads to the value 2,9. If we assume this same supposition, we shall find b_g to be equal to circa 920 also for the critical isothermal. But b_0 will be found to be considerably higher than at 0°. We saw above that the difference amounts to 77 units for 99° difference in temperature. We shall therefore find b_0 at — 242° C. from the equation:

$$b_0 = 463 + \frac{242}{99} \times 77 = 463 + 188 = 651.$$

If therefore we put $b_g = 920$ and $b_0 = 650$, then in the first place b_g is no longer equal to $2 b_0$, but to:

$$b_g = 1,415 b_0.$$

The variability of b is therefore much smaller than at 0°, and in consequence of this the quantities β_1 and β_2 will also be found to be much smaller, and the critical quantities will approach still more closely to the normal values.

The quantity $\mu = \frac{b_0}{b_g - b_0}$ is here $\frac{1}{0,415} = 2,41$, and the value of $x = \left(\frac{b_k - b_0}{b_g - b_0} \right)^2$ of equation b ceases accordingly to be 0,709, but becomes 0,852. In consequence of this we find:

$$\frac{b_k - b_0}{b_g - b_0} = \sqrt{0,852} = 0,923,$$

from which follows:

$$b_k = 0,977 b_g = 899.$$

For v_k and for $\beta_1 + \beta_2$ we find (comp. § 3):

$$v_k = 2,87 b_k \quad ; \quad \beta_1 + \beta_2 = 0,0228.$$

So we find:

$$v_k = 2,87 b_k (= 2,80 b_g = 3,97 b_0) = 2579,$$

a volume which is reached at 0° C. at a pressure of ± 550 atm.

The values of β_1 and β_2 taken separately are:

$$\beta_1 = \frac{(1-x)^2}{2-x+x^2} = \underline{0,0117} \quad ; \quad \beta_2 = \underline{0,0111}.$$

¹⁾ Zie VAN DER WAALS, l. c. III, p. 647.

Now we return to the experimental verification of v_k .

1 Gr. H_2 at 0° C. and 1 atm. occupying a space of 11127 cM³, v_k is expressed in ccM³. equal to $2579 \times 10^{-6} \times 11127$, hence the critical density is:

$$d_k = \frac{1}{28.70} = \underline{0,0348}.$$

According to the theorem of the straight diameter of MATHIAS we have:

$$\frac{d_1 + d_2}{d_k} - 2 = \left(1 - \frac{T}{T_k}\right) \varphi,$$

which quantity φ has been found by YOUNG and MATHIAS to differ little from unity for different non-associating substances.

DEWAR¹⁾ found the density of the liquid phase at the melting point of H_2 ($16^\circ,5$) to be 0,086, so we find, neglecting the density d_2 of the vapour:

$$\frac{0,086}{d_k} - 2 = 1 - \frac{16,5}{31,0} = 0,468,$$

which yields for d_k :

$$d_k = \frac{0,086}{2,468} = \underline{0,0348},$$

in perfect agreement with the value of d_k we have calculated above.

We now proceed to the calculation of the other critical quantities T_k , p_k , X and Y .

We find for T_k :

$$RT_k = \frac{8}{27} \frac{a}{b_k} \times \frac{0,9549 \times 1,0456}{0,9883} = 1,010 \times \frac{8}{27} \frac{a}{b_k} = 0,299 \frac{a}{b_k}.$$

With $a = 300$, $b_k = 899$ we find therefore

$$0,9994 \frac{T_k}{273} = 0,100.$$

so

$$\underline{T_k = 27^\circ,2}.$$

This value is somewhat too low; the experiment has yielded $T_k = \pm 31^\circ$.

We find for the critical pressure:

$$p_k = \frac{1}{27} \frac{a}{b_k^2} \times \frac{0,9439 \times 1,093}{0,9883} = 1,044 \times \frac{1}{27} \frac{a}{b_k^2} = 0,0387 \frac{a}{b_k^2}.$$

¹⁾ l. c. bl. 477. DEWAR finds the melting point to be 16° à 17° ; the critical temperature to be 30° à 32° absolute temperature. [The density of the liquid phase at the boilingpoint (20° à 21°) has been estimated to be $\pm 0,07$, but then the vapour density may no more be neglected.]

With the values found for a and b_k we get:

$$\underline{p_k = 14,4 \text{ atm.}}$$

DEWAR found ± 15 atm.

The critical coefficient X becomes:

$$X = \frac{3}{8} \times \frac{0,9439}{0,9549} = \frac{3}{8} \times 0,989 = \underline{0,371},$$

so nearly the normal value 0,375.

For $Y = \left(\frac{T}{p} \frac{dp}{dT} \right)_k$ we find now another value than before. In the general expression ¹⁾

$$\frac{T}{p} \left(\frac{dp}{dT} \right)_v = 1 + \frac{1}{p} \left[\frac{a}{v^2} + \left\{ \left(\frac{dP_b}{db} \right)_t - T \frac{d^2 P_b}{dT db} \right\} \frac{db}{dv} \right]$$

the factor of $\frac{db}{dv}$ is now no longer zero. For as $\frac{dP_b}{db} = a(b-b_0)$, we have:

$$T \frac{\partial}{\partial T} \left(\frac{dP_b}{db} \right) = -T a \frac{db_0}{dT},$$

as we found a to be independent of T , b_0 on the other hand to depend upon T . We find therefore for the factor of $\frac{db}{dv}$:

$$a \left(b - b_0 + T \frac{db_0}{dT} \right).$$

We have found above: $b_g - b_0 = \sqrt{\gamma} T$, so $b_0 = b_g - \sqrt{\gamma} T$, and as b_g has been found to be nearly independent of T , we get

$$T \frac{db_0}{dT} = -\frac{1}{2} \sqrt{\gamma} T = -\frac{1}{2} (b_g - b_0).$$

The factor of $\frac{db}{dv}$ becomes therefore:

$$a \left(b - b_0 - \frac{1}{2} (b_g - b_0) \right),$$

and with

$$a = \frac{RT}{(b_g - b_0)^2} = \frac{\left(p + \frac{a}{v^2} \right) (v - b)}{(b_g - b_0)^2} = \left(p + \frac{a}{v^2} \right) \left(\frac{v - b}{b - b_0} - 1 \right) \frac{1}{b - b_0}$$

— as according to (1) we have $\frac{1}{(b_g - b_0)^2} = \frac{1}{(b - b_0)^2} \left(1 - \frac{b - b_0}{v - b} \right)$ —

we get:

¹⁾ v. D. WAALS, l. c. III, p. 644.

$$\left(\rho + \frac{a}{v^2} \right) \left(\frac{v-b}{b-b_0} - 1 \right) \left(1 - \frac{1}{2} \frac{b_g - b_0}{b - b_0} \right).$$

This expression for $\left(\frac{T}{p} \frac{dp}{dT} \right)_k$ becomes therefore, if we put $\frac{db}{dv} = \beta_1$:

$$\left(\frac{T}{p} \frac{dp}{dT} \right)_k = \left(1 + \frac{a}{\rho_k v_k^2} \right) \left[1 + \beta_1 \left(\frac{v_k - b_k}{b_k - b_0} - 1 \right) \left(1 - \frac{1}{2} \frac{b_g - b_0}{b_k - b_0} \right) \right].$$

This yields with the values calculated above (see § 3):

$$Y = 4 \times \frac{0,9772}{0,9439} \left[1 + 0,0117 \left(\frac{1680}{249} - 1 \right) \left(1 - \frac{1}{2} \cdot \frac{270}{249} \right) \right] = \\ = 4 \times 1,035 [1 + 0,0117 \times 5,747 \times 0,4578],$$

or

$$Y = 4,140 \times 1,0308 = \underline{4,267}.$$

Finally we investigate, whether this value of $\left(\frac{T}{p} \frac{dp}{dT} \right)_k$ may be brought into agreement with the few experimental data of DEWAR. DEWAR found namely (l.c.):

$$T = 20^\circ \text{ à } 21^\circ \quad | \quad p = 1 \text{ atm.}$$

$$T_k = 30^\circ \text{ à } 32^\circ \quad | \quad p_k = 15 \text{ atm.}$$

The two data yield by means of the integral formula

$$nep \log \frac{p_k}{p} = f \left(\frac{T_k}{T} - 1 \right)$$

for f the value:

$$f = \frac{nep \log 15}{\frac{12}{20} \text{ à } \frac{9}{21}} = 2,708 \times \left(\frac{5}{3} \text{ à } \frac{7}{3} \right),$$

according as we take 20° and 32° or 21° and 30° . The lowest value is 4,51, so still higher than the calculated value 4,27. We must further note that 20° differs comparatively very much from T_k (being $\frac{2}{3} T_k$) and that therefore at 20° the factor f will certainly be found to be greater than near T_k , hence 4,51 is probably too great.

From the above we may in any case conclude, that the large extrapolation, by means of which we have calculated the value of b_0 at -242° from the values of b at 0° , 100° and 200° , really yields the critical data with a sufficient degree of accuracy — at least in so far as we may judge from the few data, that are available. Only Y is probably too low.

We have reason to expect a priori that the new equation, derived by VAN DER WAALS for the variability of b with the volume, does

not represent the experimental data with perfect accuracy. For the correction, introduced before for the partial coincidence of the distance spheres has not been taken into account in the deduction of this formula. The quantity b in $r - b$ for a monatomic gas, e. g. mercury vapour, argon etc. would according to the new theory of VAN DER WAALS remain invariable; whereas this quantity which according to the former considerations would for very large volumes be equal to four times the molecular volume, for smaller volumes would certainly have a smaller value, and it would approach to about twice the molecular volume — at least if the shape of the molecules does not exercise any influence on this calculation.

Physics. — “*Peculiarities and changes of Fraunhofer lines interpreted as consequences of anomalous dispersion of sunlight in the corona*” by Prof. W. H. JULIUS.

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

Especially by JEWELL's investigations on the coincidence of solar and metallic lines¹⁾ attention has been drawn to several variable peculiarities of Fraunhofer lines. Here we do not mean the irregularities occurring in the spectrum of spots or of faculae, which relate to disturbances in comparatively small parts of the sun, but abnormalities shown by the average sunlight, as observed when the slit is illuminated by a long strip of an imperfectly focused solar image. In that case, according to DOPPLER's principle we may, of course, expect displacements of the lines in consequence of the Sun's rotation, of the rotation of the Earth, and of the change in the distance between Sun and Earth caused by the excentricity of the Earth's orbit. But even when all these influences have been allowed for, some irregularities still remain.

Indeed, JEWELL has observed that some Fraunhofer lines do, others do not, exactly coincide with the emission lines in the arc spectrum of elements, and that the displacements are unequal both for lines of different elements and for the various lines of one and the same element. Moreover, the shifting of certain lines on one set of photographic plates was sometimes found different from that on a set of

¹⁾ L. E. JEWELL, “The coincidence of solar and metallic lines. A study of the appearance of lines in the spectra of the electric arc and the Sun.” *Astroph. Journ.* III p. 89—113, 1896. The same: “Spectroscopic notes. Absolute wave-lengths, spectroscopic determinations of motions in the line of sight, and other related subjects.” *Astroph. Journ.* XI p. 234—240, 1900.

plates taken at another time. With several lines the intensity too appeared to be variable.

JEWELL explains these phenomena on certain hypotheses on density, pressure and temperature of the absorbing and emitting gases in the different layers of the solar atmosphere, and by variable ascending and descending velocities of matter.

HALE'S abnormal solar spectrum.

Much greater than the irregularities mentioned are those, found in an "abnormal" solar spectrum, lately described by G. E. HALE.¹⁾

This highly remarkable spectrum had accidentally been photographed as long ago as February 1894 in a series of exposures made with the sole intention of investigating the peculiarities of the grating. Only a few months later it was discovered that a very extraordinary phenomenon had been photographed. HALE hesitated to publish this accidental discovery. Copies of the plate were sent to several spectroscopists for examination with the request that an explanation, referring the phenomenon to some origin other than solar, might be supplied, if possible. As no such explanation was forthcoming, the spectra were very carefully measured and described.

On one and the same plate 12 exposures had been successively made in the third order spectrum of a plane grating. A solar image of 51 m.m. in diameter was so adjusted that the image of a spot fell exactly on the slit. The length of the slit (6.5 m.m.) corresponded to about one eighth of the sun's diameter.

The first exposures show the normal spectrum without any considerable changes. Then came the disturbance, which culminated in the eighth spectrum and, in the following four, decreased rapidly. HALE gives reproductions of four spectra, each of them extending from 2 3812 to 2 4132. N^o. 1 has been taken before the disturbance occurred; N^o. 2 is the most abnormal spectrum; N^o. 3 is called by HALE the "intermediate" spectrum, it has been obtained a few moments after the abnormal one; N^o. 4 shows once more the normal solar spectrum, as it was photographed at another time on another plate. Nos. 1, 2 and 3 show a dark band throughout the whole spectrum, corresponding to the sun-spot which had been focused on the slit.

The most prominent features of the abnormal spectrum are :

1^o. The band due to the spot appears much fainter than in the spectra, photographed before and after the disturbance.

¹⁾ GEORGE E. HALE. "Solar research at the Yerkes Observatory". *Astroph. Journ.* XVI p. 211—233, 1902.

2°. With several Fraunhofer lines the intensity or the width is greatly diminished. This is most conspicuous with the broad, dark calcium bands H and K and with the hydrogen line H δ , these being almost totally absent in the abnormal spectrum.

3°. Other lines, on the contrary, appear uncommonly strengthened.

4°. Many lines are more or less displaced.

The same peculiarities are noticed, though generally in a smaller degree, in the intermediate spectrum, so that the latter, in fact, forms a link between the abnormal and the normal spectrum.

This marvellously complicated disturbance was not confined to light coming from a comparatively small part of the solar disk, for instance from the immediate surroundings of a spot; on the contrary, it extended almost equally over the whole width of the spectrum and was therefore nearly the same for all the light which came from a very great area of the Sun.

The moments of the 12 exposures and the exact date had not been recorded, but there was sufficient evidence that the whole process of the disturbance lasted only a very short time.

HALE calls the phenomenon: "a remarkable disturbance of the reversing layer". But is it not almost impossible to imagine a rather thin layer in the solar atmosphere undergoing suddenly and simultaneously over a great part of the sun such a thorough change, as to make its absorbing and radiating power in some parts of the spectrum for a while nearly unrecognizable?

It occurred to me, therefore, that the origin of the phenomenon should be looked for somewhere on the path of the light between the Sun and the Earth. If on this path there be media, causing anomalous dispersion, the beam must show an altered composition.

As I formerly indicated ¹⁾, the properties of the chromospheric light may be derived from the supposition, that this light has been scattered out of the photospheric light by anomalous dispersion. According to this hypothesis the spectrum of the chromosphere informs us, which are the kinds of light, that may follow rather strongly curved paths in the solar atmosphere. So the idea suggested itself, that the same waves might play a striking part in HALE'S abnormal spectrum.

In order to investigate the question as impartially as possible, I marked (before consulting HALE'S table or a table of chromosphere

¹⁾ Proc. Roy. Acad. Amst. II, p. 575—588; III, p. 195—203; IV, p. 162—171; *Physikalische Zeitschrift* 4, p. 132—136.

TABLE I.

Lines whose intensity is less in the abnormal than in the normal spectrum.

Wavelength	Intensity				Elements	Remarks.
	normal	inter- mediate	abnormal	Chromo- sphere		
	(ROWLAND)	(HALE)	(HALE)	(LOCKYER)		
3871.4				4	<i>C</i>	Not mentioned in HALE's list, but distinctly weakened in the abnormal spectrum on the reproduction.
3872.6				4	<i>Fe</i>	
3874.09	4	9	—	2 (†)	<i>Fe</i>	
3878.47	22	25	—	3 3	<i>Fe, Fe</i>	
H_5 3889.05	?	15	—	8	<i>H</i>	
3895.80	7	12	—	3	<i>Fe</i>	
3899.30	5	4	—	2	<i>V?</i>	
3903.09	10	12	—	2—3	<i>Fe</i>	
3905.66	12	20	—	2	<i>Cr, Si</i>	
3906.70	14	—	4	2	<i>Fe</i>	
3913.63	9	7	—	6	<i>Ti</i>	* These intensities are very probably estimated too high when compared with the numbers in the second column. Cf. the Note on p. 593.
3914.49	7	8	5*		<i>Ti</i>	
3916.54	3	—	4*	3	<i>V</i>	
3920.41	10	10*	10*	3	<i>Fe</i>	
3923.05	12	12*	12*	3	<i>Fe</i>	
K 3933.82				10	<i>Ca</i>	
3944.46	15	15*	12*	5	<i>Al</i>	
3948.91	13	15	—	3	<i>Fe</i>	
3950.40	5	—	2	3	<i>Fe</i>	
3953.02	17	15	—		<i>Fe, etc.</i>	
3958.35	5	8	—	4	<i>Ti</i>	
3961.67	20	20	—	6	<i>Al</i>	
H 3968.63	(700)	7	7	10	<i>Ca</i>	
H_e 3970.48	7	8	—	10	<i>H</i>	
3977.89	6	8	—	2	<i>Fe</i>	
3986.90	6	8	—			
3998.78	4	4	4*	4	<i>T</i>	
4012.50	5	4	5*	5—6	<i>Ti, etc.</i>	
4033.22	7	12	3	3—4	<i>Mn, Fe</i>	
4034.64	6	10	—	3—4	<i>Mn, Fe</i>	
4045.98	30	30	5	7	<i>Fe</i>	
4063.76	20	20	—	6—7	<i>Fe</i>	
4071.91	15	15	15*	6	<i>Fe</i>	
4077.88	8	10	7*	10	<i>Sr</i>	
H 4102.00	40	7	—	10	<i>H</i>	

lines) on the reproductions of the spectra in the *Astrophysical Journal* a number of lines, which struck me as being weakened in the abnormal spectrum. By means of GEORGE HIGGS' photographic atlas of the normal solar spectrum the wave-lengths of the selected lines were easily read; they are to be found in the first column of Table I.

The second, third, and fourth columns show the intensities of these lines in the normal, the intermediate, and the abnormal spectrum as given by HALE (for the normal spectrum from ROWLAND'S tables, for the other two from estimations by Mr. ADAMS). HALE remarks that the intensities of the lines were estimated independently for the two disturbed spectra¹⁾. The fifth column indicates the intensities of corresponding chromosphere lines as found by LOCKYER in

TABLE II.

Lines whose intensity is greater in the abnormal than in the normal spectrum.

Wave-length	Intensity.				Elements.	Remarks.
	normal (ROWLAND)	inter- mediate (HALE)	abnormal (HALE)	Chromo- sphere (LOCKYER)		
3921.86	4	—	20		Zr, Mn	
3927.77	—	—	25		?	
3930.45	8	15	28	3-4	Fe	
3937.39	—	—	40		?	
3940.25	—	7	42		?	
3950.50	2	—	43		V	
3962.29	3	—	41		Fe?	
3973.77	6	—	45	2?	Ni, Zr, Fe, Cu	
3981.92	4	13	30	6*	Ti, Fe	* In HUMPHREYS' table of chromosphere lines (1901 eclipse) this line does <i>not</i> occur.
3992.97	3	4	40		V, Cr.	
3996.80	—	—	9		?	
4013.90	8	42	45		Ti, Fe	
4014.67	5	9	20		Fe	
4023.38	—	—	40		?	
4033.77	2	3	45		Mn	
4040.79	3	6	20	4	Fe	
4044.09	5	20	45		Fe	

¹⁾ In selecting the lines that appeared weakened in the abnormal spectrum I did of course compare the three spectra mutually. That is why in my table some lines occur, whose intensities, as estimated by Mr. ADAMS, are not comparatively low in the abnormal spectrum.

the spectrum, secured at Viziadrug during the 1898 eclipse¹⁾; the sixth column shows the absorbing substances.

In a similar way Table II has been composed; here we find the lines, which on the reproduction appeared to be strengthened in the abnormal spectrum.

The result is very striking. Weakened lines correspond to chromosphere lines, almost without exception; most of the strengthened lines, on the other hand, are not to be found in the spectrum of the chromosphere.

LOCKYER gives the strength of the chromosphere lines on a scale such that 10 indicates the strongest and 1 the faintest lines. If we take into account that in his list the greater part of the lines bear the numbers 1 and 2, our table shows us, that by merely observing the abnormal solar spectrum we have been able to pick out strong chromosphere lines. This cannot be chance. Undoubtedly both phenomena — the weakening of Fraunhofer lines in the abnormal spectrum and the origin of the chromosphere spectrum — are to be explained in close relation with each other.

The strengthening of lines in the abnormal spectrum does not, on the contrary, seem to be so directly connected with the composition of the chromosphere spectrum.

If our view be correct that the chromospheric light has been separated by strong ray-curving from the "white" light emitted by deeper layers, those special radiations must, as a rule, show reduced intensity in the spectrum of the Sun's disk²⁾. Fraunhofer lines cor-

1) LOCKYER, CHRISHOLM-BATTEN and PEDLER. "Total Eclipse of the Sun, January 22, 1898. — Observations at Viziadrug," *Phil. Trans., A*, vol. 197, p. 151—227, 1901.

2) It might be thought that the rays forming the chromosphere light, need to be absent only from the spectrum of the edge but not from that of the central portions of the Sun's disk. By a simple consideration, following from a look at Fig. 4 of my paper, read in Febr. 1900 (*Proc. Roy. Acad. Amst. II*, p. 580) we see, however, that the chromosphere light visible to us may very well, for a part, have its origin even in points of the Sun which lie opposite to the Earth's direction. The chromosphere light, reaching the Earth, may proceed from any point of SCHMIDT's "critical sphere". For the greater part it is likely to come from the back half of the Sun. But then the half, facing us, furnishes the chromospheric light which travels to other regions of the universe, and this light, of course, is wanting in the spectrum of the disk. (There is some reason for supposing that, on an average, more chromospheric light is sent forth in directions making great angles with the Sun's equator, than to the equatorial regions, including the Earth's orbit.)

responding to chromosphere lines will therefore have a more or less darkened background in the ordinary solar spectrum. The rate of darkening at various distances from the centre of an absorption line is, of course, connected with the shape of the dispersion curve near that line; whereas the average shading depends 1st on the quantity of matter causing anomalous dispersion and 2^{ndly} on the slopes and the directions of the density gradients in the gases through which the light is transmitted, viz. on the Sun's "activity" ¹⁾.

We distinguish, therefore, a twofold origin of the dark lines in the solar spectrum: real absorption of those waves, exactly corresponding to the periods of the media, and dispersion of the strongly deviated neighbouring light ²⁾.

The dispersion will be especially evident where extraordinary differences in the density of the medium occur; in this way the widening of most of the Fraunhofer lines in the spectra of spots may be accounted for.

Dispersed light has not, of course, vanished; the absence of certain rays in the spectrum of a spot is counterbalanced by the increased intensity of the same radiations in the light coming from the neighbouring faculae. Thus the distribution of the density in the solar gases may locally be such, that a limited part of the disk seems to emit a considerable amount of rays with abnormally high or abnormally low refractive indices. In the spectrum of such parts not only will the Fraunhofer lines show narrower and fainter than usually, but here we may even meet with lines contrasting brightly with their surroundings. These bright lines will not coincide with the corresponding absorption lines; their average wave-length will in general be greater or smaller than that of the absorbed light, for, according to the accidental distribution of the density, we shall find either the rays with high or those with low refractive indices most prominent in the beam.

The above considerations suggest an explanation of HALE's abnormal spectrum.

In fact, the lines showing especially faint in this spectrum were exactly those, causing strong anomalous dispersion — witness the

¹⁾ The possible influence of the general or regular ray-curving (after SCHMIDT's principle) on the feature of the spectral lines has, in the present paper, been left out of consideration. If we were able to observe or to calculate the radii of the "critical spheres" for radiations undergoing anomalous refraction, it would be possible to estimate that influence; but as yet sufficient data are wanting.

²⁾ Proc. Roy. Acad. Amst. II. p. 580.

chromosphere spectrum. With H , K , H_2 and some iron lines it is conspicuous that the abnormal faintness regards mainly the broad dark shadings of the lines, i. e. those parts, whose darkness in the normal spectrum we attributed not to absorption, but to dispersion. Moreover, the dark band due to the spot has nearly disappeared. This means that waves, which in normal circumstances are wanting in the spot spectrum on account of their strong dispersion, at the time of the disturbance had been gathered again into the beam reaching the instrument.

How all this may happen will become evident as soon as we shall be able to establish a plausible cause, by which, within an angular space great enough to include a considerable part of the solar disk, the strongly dispersed rays might be gathered again.

It is not necessary to introduce a new hypothesis for the purpose. The same idea about the Sun's constitution¹⁾ which enabled us to explain the properties of the chromosphere and the prominences, furnishes us once more with the required data.

Indeed, if (according to SCHMIDT's theory) the Sun is an unlimited mass of gas, surfaces of discontinuity must exist similar to those, whose general feature has been determined by EMDEN²⁾ for a sharply outlined radiating and rotating sun. These surfaces must extend unto the remotest parts of the gaseous body — a conclusion in excellent harmony with the visible structure of the corona. For along the surfaces of discontinuity waves and whirls are formed; the core-lines of the vortices nearly coincide with the generatrices of these surfaces of revolution, and in these cores the density is a minimum. This may account for the streaky appearance, shown more or less distinctly in all good photographs and drawings of the corona.

This particular appearance may have another cause, though; for what follows, however, this is immaterial. We only assume that the density of the coronal matter varies in such a way, as to correspond to the striped structure visible at the time of a total eclipse of the Sun.

A coronal streamer which, at a given moment, runs exactly in the direction of the Earth may be very roughly compared, then, to a bundle of glass tubes through which we are looking lengthwise. Such a structure will gather and conduct rays of various directions, entering it at one end. This takes place also if the parts with the greater and those with the smaller optical density do not alternate abruptly, like glass and air, but gradually.

¹⁾ Proc. Roy. Acad. Amst. IV, p. 162.

²⁾ R. EMDEN, Beiträge zur Sonnentheorie, Ann. d. Phys. [4], 7, p. 176—197.

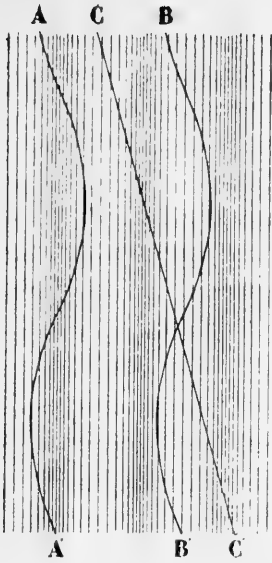


Fig. 1.

In Fig. 1 the optical density of the matter may be represented by the compactness of the streaking. A ray for which the medium has a large positive refractionconstant would for instance follow the path AA' , curving round the denser parts of the structure; a ray BB' , for which the medium possesses a large negative refractionconstant, would move in a similar way through the more rarefied regions. On the other hand, the light CC' for which the constant exactly equals zero is not influenced by the fluctuations of the density; and if for some kind of light the refractionconstant is very nearly zero, the ray would have to travel a long way almost parallel to the structure before its curving would be perceptible.

Now the corona sometimes shows exceedingly long, pointed streamers. We only have to suppose that the Earth was exactly in the direction of such a streamer at the moment the abnormal spectrum was photographed; then all the irregularities observed in this spectrum become clear. Light, under normal circumstances absent from the solar spectrum through strong dispersion, has been collected by the coronal streamer; hence the weakening of the Fraunhofer lines, especially also of those in the spectrum of the spot. As the abnormalities were caused by a peculiar distribution of matter in the vast regions of the corona, lying between the source of light and the Earth (and not by disturbances in a relatively thin "reversing layer") they could appear in the same way over a great part of the Sun's disk. The rarity of the phenomenon is the result of the slight chance we have to take a photograph at the very moment on which an uncommonly long coronal streamer is projected exactly on the part of Sun's disk illuminating the slit; the short duration finally is a consequence of the difference between the angular velocity of the corona and that of the Earth in its orbit.

As we have mentioned before, *no* chromosphere lines correspond, in general, to those lines showing extraordinarily *strong* in the abnormal spectrum. How are we to account for the strengthening of these lines?

We might be tempted to think of absorption in the corona; for if it be true that a streamer was turned towards the Earth, the rays had to go an uncommonly long way through an absorbing medium. But on closer examination this idea is less probable.

The particles of the extremely rarefied corona gases will hardly influence each other; their periods will, therefore, be almost absolutely constant, so as to cause very sharp, narrow absorption lines. Thus it is difficult to understand, how an absorption line, already present in the normal solar spectrum, might be strengthened by the absorbing power of the corona. Further, in studying HALE'S table, we observe that many lines which are strong in the abnormal spectrum, show a much smaller intensity in the intermediate spectrum (taken only a few moments later); whilst the reverse happens as well, viz. that lines are strong in the intermediate and very weak in the abnormal spectrum. This hardly fits in with the absorption hypothesis. Some lines showing this peculiarity are given in table III.

TABLE III.

Lines whose intensity is very different in the intermediate and the abnormal spectrum.

Wave-length	Intensity.				Elements	Remarks.
	normal	intermediate	abnormal	chromosphere		
	(ROWLAND)	(HALE)	(HALE)	(LOCKYER)		
3905.66	12	20	—	2	<i>Cr, Si</i>	
3905.81	21	—	20		<i>Si</i>	
3921.71	9	14	—		<i>Ti, La, Zr, Mn</i>	
3921.87	4	—	20		<i>Zr, Mn</i>	
3950.33	—	10	—		?	
3950.51	2	—	13		<i>Y</i>	
3972.30	2	12	—		<i>Ni</i>	
3972.61	2	—	12		?	
4005.86	3	25	5		?	
4057.39	4	—	15	1—2	<i>Co, Fe</i>	
4057.66	7	10	—		?	

In the chromosphere spectrum corresponding lines seem to be wanting. (At 2 3905.66 and 2 4057.39 the faint chromosphere line may possibly belong to another element than the abnormally strengthened absorption line).

To arrive at a more satisfactory explanation of the strengthening-phenomenon we suppose that these absorption lines do indeed cause anomalous dispersion of neighbouring waves, but in a very slight

degree. Then, the refractive indices of the neighbouring waves differing hardly from unity, the direction of those rays will only be perceptibly changed after they have travelled a very long way through the corona and almost parallel to its structure-lines. Whereas the strongly refracted rays, entering the coronal streamer in various directions, were obliged to follow the structure-lines, curving about them, and so in a sense were concentrated on the Earth, it may happen with the extremely slightly curved rays we are now considering, that they have been bent for instance only once over the whole length of the streamer and continue their way in a direction not meeting the observing station. The divergence of a beam consisting of these rays will have increased, the intensity diminished. Thus, the resultant spreading of neighbouring light causes the absorption line to appear somewhat widened and therefore strengthened. But obviously it must be possible too, that, after a short time, under the influence of another part of the corona, circumstances turn out even favourable for that slightly curved light to reach the observer. In that case the absorption line is weak again. (Similar alternations, of course, also occur with the more strongly refracted rays, and that in quicker succession, but this does not alter the fact of their *average* intensity appearing increased as long as the structure lines of the coronal streamer are turned towards the spectroscope. For a detailed discussion of this case see the Note at the end of this paper).

In both abnormal spectra a number of absorption lines are more or less displaced. Perhaps this is partly due to motion in the line of sight; but after the foregoing it will not be necessary to explain in detail, that also anomalous dispersion can account for this phenomenon. Dissymmetric form of the dispersion-curve as well as a peculiar distribution of the density of the coronal matter may unequally affect the intensity of the light on both sides of the absorption line, and thus bring about a seeming displacement of the line.

Certain peculiarities of lines in the normal solar spectrum.

If we have been right in connecting the uncommonly great abnormalities in HALE'S spectrum with a very particular position of the Earth with respect to the corona, it is to be expected that similar irregularities, though to a smaller degree, will ever be found, as the sunlight always reaches us through the corona.

According to JEWELL'S above mentioned investigations this supposition proves to be well founded. Many solar lines have varying intensities and positions, so that JEWELL deems them unfit for standards for

very accurate determinations of wavelengths. And these are for the greater part the most prominent lines of the spectrum, especially the shaded ones¹⁾.

JEWELL emphasizes the fact that all distinctly shaded lines in the solar spectrum show to a greater or less degree the following typical feature²⁾.

Within a broad, shaded, moderately dark background a much darker central absorption line contrasts rather sharply (Fig. 2).



Fig. 2

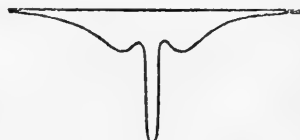


Fig. 3.

Besides, the absorption curve often shows dippings close to the central line, as in Fig. 3, sometimes symmetrical, sometimes dissymmetrical. JEWELL affirms that this is not an optical delusion, due to contrast, but a real phenomenon. He assumes, therefore, that the broad absorption band is produced in the lower portions of the solar atmosphere and under a great range of pressure; that in higher levels radiation prevails again, producing a rather wide emission line; and that finally in the highest parts, where the pressure is very much less, the sharp absorption line is produced. The position of this central absorption line with respect to the emission line is usually unsymmetrical, which is conspicuous in the case of *H* and *K*. The central line itself also varies somewhat in width upon different plates and its maximum of intensity is not always in the middle of the line. The displacement of this central line in *H* and *K* varies in magnitude, but, so far as has been observed, always toward the red with respect to the emission line and the corresponding metallic line (in the arc).

JEWELL concludes that the absorbing calcium vapour descends all over the solar surface with a velocity sometimes amounting to about 75 miles per minute.

Upon the same plates showing strong dissymmetry in *H* and *K*, the shaded lines of other elements (*Fe*, *Al*, *Mg*, *Si*) have been examined. The strongest iron lines and one aluminium line showed displacements of the same character as that observed in the case of

¹⁾ *Astroph. Journ.* XI, p. 236, 1900.

²⁾ JEWELL, "Certain peculiarities in the appearance of lines in the solar spectrum and their interpretation". *Astroph. Journ.* III, p. 99, 1896.

H and *K*, but to a much smaller degree and sometimes toward the violet, sometimes toward the red. Certain shaded lines of *Mg* and *Si*, on the contrary, showed no evidence of a displacement, nor did the iron lines without considerable shading, the faint calcium line at λ 3949,056 and many other lines.

If we admit no other explanation of line-shifting and -widening besides those, based on DOPPLER'S principle and on the effect of pressure and temperature, we arrive at very strange conclusions relative to the condition of the elements in the solar atmosphere. Not less surprising is, as noticed by JEWELL¹⁾, the small amount of the absorption in the shaded parts of the lines, when we consider the enormous depth of the solar atmosphere and the high pressure which must exist in the absorbing layers, for them to produce a broad absorptionband.

By making various suppositions concerning the condition of the gases in the solar atmosphere, JEWELL succeeds in finding an interpretation of most of these astonishing facts. But it must be granted that his explanations include a greater number of arbitrary and mutually independent hypotheses than is the case with our explanations, founded as they are on selective ray-curving and readily deduced from that principle for each separate phenomenon, without introducing new suppositions.

Only the dark central lines of the Fraunhofer lines are to be ascribed, in our theory, to real absorption. Their shaded background of varying intensity we consider as an effect of anomalous dispersion of the not absorbed neighbouring waves. This selective scattering will be strongest in those places where the density-gradients are relatively steep, viz. in whirls in the deeper regions of the gaseous body. But some of the widely dispersed rays may be gathered by the corona owing to its "tubular" structure and be conducted along its greater or smaller streamers.

This will especially apply to the most strongly refracted waves, whose position in the spectrum is very close to the real absorption lines; thus pseudo emission lines are produced in about the middle of the pseudo absorption bands.²⁾

¹⁾ Astroph. Journ. III, p. 106.

²⁾ A most remarkable fact is that the shading of *K*, *H*, the iron-line λ 3720,086 and of some other strong shaded lines is sometimes partially broken up into a series of faint nebulous lines, symmetrically situated about the central line. In each case the distance apart of the component lines increased as the distance from the center increased (JEWELL, Astrophysical Journal 8, p. 51—53).

It might have been predicted by our theory that we should meet with this phenomenon now and then.

Most likely HALE's abnormal spectrum has shown us a case, where these seeming emissionbands acquired an uncommon extent. We may therefore expect that a systematical investigation of solar spectra, photographed at different times, will afford all kinds of intermediate cases.

It would be desirable, for the moments when the photographs are taken, to know form and position of the coronal streamers extending toward the Earth. At all events the actual phase of the sun-spot period, with which the shape of the corona seems to be connected, should be taken into consideration; and perhaps the simultaneous observation of the photospheric reticulation, discovered by JANSSEN, may procure some evidence concerning the position of coronal streamers, and thus contribute to our knowledge of their influence on the Fraunhofer spectrum.

Mineralogy. — "*On the refractive index of rock-glasses,*" by P. TESCH:
(Communicated by Prof. J. L. C. SCHROEDER VAN DER KOLK).

Of the group of the igneous rocks, the origin of which out of fluid red-hot condition we accept, the volcanic rocks constitute that subdivision, which includes the rocks, that as lavas have broken through the surface of the earth.

The quick cooling at the atmosphere renders it possible that in these rocks part of the magma congeals amorphyously, so that next to the minerals a rockglass appears, which constitutes either an inferior part or a prevailing one of the rocks. So in general this glass

Let us consider a beam of light of an exactly defined wavelength belonging to the shaded background of an absorption line. This beam leaves the deeper layers of the Sun with a certain divergence. As it passes along a "tube" of the corona, its divergence will alternately diminish and increase, and on reaching the Earth it shows in the spectrum an intensity, depending on the divergence (or perhaps convergence) with which it has left the last traces of the corona. For a beam of light whose wavelength is only slightly nearer to that of the absorption line, the medium will have a considerably greater refraction constant, so that the rays of this beam, on their way through the corona, may make part of a bend more than the former ones. The beam may therefore arrive with a quite different degree of divergence and, consequently, of intensity. Thus, proceeding towards the absorption line from either side, we easily see that we must meet with a periodically changing intensity. Rays, corresponding to the middle of one of the so formed fringes, will have made one full bend more or less than the rays, belonging to the middle of the next fringe.

If this interpretation be correct, the width and the number of fringes visible must prove to be variable. As far as I know, the observations made on this point are not numerous. May the proposed views serve to further the investigation of this interesting phenomenon.

consists of silica and metal-oxides. We may suppose that the silica, which is most likely to be the principal part, will also have a prevalent influence on the physical characters of such natural glass.

A determination of the specific gravity of the glass is made more difficult by the presence of many gas-bubbles. If this obstacle did not exist, the specific weight would be a better expedient for a quick temporary orientation than the determination of the refractive index, for which more instruments are necessary. With respect to the specific gravity it could be stated, that with these rocks where the value of the index the use of bromoform as liquid of comparison necessitated and whose exponent proved to be greater than that of bromoform (1,593), the specific gravity of the glass was still higher than that of bromoform (2,88). The small air-free, not to be isolated grains, still sank in this liquid. Now I have tried to find out in how far the refractive index is dependent on the SiO_2 percentage. For that purpose 16 rocks have been examined, forming a series of the most acid to the most basic magmas, which occur in nature.

The result has been comprised in the following table:

Name	Origin	SiO_2	Index
Granite	Magurka, Hungary	72,65	1,500
Granite	Brocken, Harz Mountains	71,19	1,500
Granite	Auvergne	70,62	1,500
Granite	Korinitzsch, Hungary	67,31	1,510
Quartzdiorite	Adamello, Tyrol	66,58	1,510
Syenite	Plauensche Grund, Dresden	60,26	1,520
Elaeolite-syenite	Ditro,	59,88	1,525
Diorite	Hodritsch, Hungary	59,57	1,525
Syenite	Ditro,	57,36	1,530
Augite-syenite	Monzoni, Tyrol	53,75	1,550
Chrysolitenorite	Radau Valley, Harz Mountains	53,64	1,550
Diorite	Auvergne	50,86	1,570
Quartzdiorite	Dumkuhlen Valley, Harz	48,89	1,585
Basalt	Dyrafjord, Iceland	48,50	1,590
Gabbro	Radau Valley, Harz	44,08	1,620
Harzburgite	Harzburg, Harz	42,24	1,630

From this we see that a classification exclusively according to decreasing SiO_2 percentage, coincides with an increasing value of the refractive index.

Apparently the metal oxides present have only little influence on that value, at least this influence falls within the limits of the errors of observation.

A chrysolite-norite and an augite syenite with about the same SiO_2 percentage have also the same index, whereas the oxides, especially MgO are sure to be there in quite another relation, for in the chrysolite-norite the minerals containing Mg come strongly to the foreground.

As regards the colour of the glass it will be almost wholly dependent on the iron-percentage.

With the examined glasses the colour changed from light green to dark brown. Just as with isomorphous mineral series, as e. g. the enstatite-hyperstene-series, the dark colour most likely points to a greater iron percentage than the light one.

The typical amorphous glassfracture can be easily distinguished at the splinters under the microscope.

The fusion of the rock-powder took place in a gasflame in which compressed oxygen was blown. As an underlayer a cupel of chalk or bone-ash was used. But care has to be taken that the melted magma of the cupel remains isolated, because there is a chance that oxides of alcaleic earths will be absorbed by the cupel and in consequence the composition of the magma does not answer any more to that of the rock. This can be obtained by directing the point of the flame towards the middle; the upperlayer then fuses quickly to a little ball, which remains isolated by the underlying rock-powder of the cupel. To control the regularity found in the independence of the refractive index of the SiO_2 percentage, two mixtures of the following composition were made:

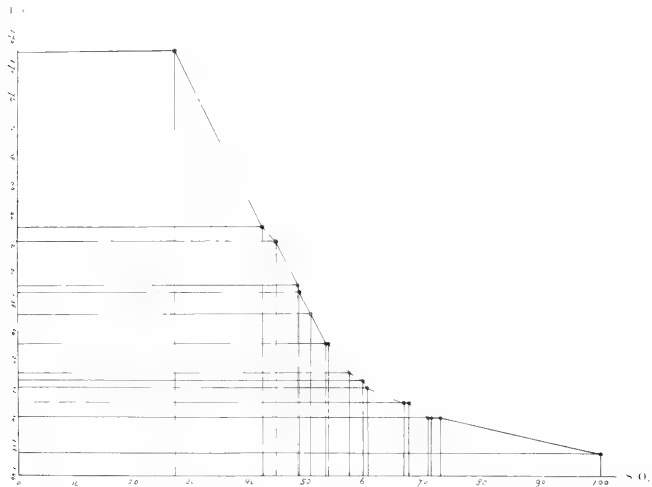
	I.	II.
SiO_2	60 %	60 %
Fe_2O_3	10	20
Al_2O_3	10	5
CaO	10	5
MgO	5	10
$\text{K}_2\text{O}, \text{Na}_2\text{O}$	5	—

Of both the mixtures the fused glass had the index 1.520; here we see again the prevalent influence of SiO_2 .

At last some slags and melted minerals were investigated.



P. TESCH. On the refractive index of rock-glasses.



Composition.	Index.
SiO ₂ 45,5	1,600
CaO 19,8	
FeO 5,3	
SiO ₂ 27,4	1,750
FeO 41,7	
CuBi 0,2	
Pb 1,5	
Al ₂ O ₃ 0,8	
ZnO 21,8	
MnO	

In this slag the ZnO plays the part of the MgO. When ZnO is replaced by MgO, the index remains the same.

Finally the index of the following minerals was determined:

Quartz	SiO ₂ 100 %	1,475
Chrysolite	" 40—45	1,610
Orthoclase	" 65	1,485

The last mineral, the pure K.Al.silicate consequently does not fit into the composed series. After mixing with some grains Fe₂O₃ (5—10 %^o) and fusing anew the index was raised to 1,510.

The method described above can be of practical use for a quick determination of the SiO₂ percentage of slags from the refractive index with an accuracy of ± 2 %^o.

A word of thanks for the aid and advice to the Professors Dr. J. L. C. SCHROEDER VAN DER KOLK and S. J. VERMAES JR. may find a place here.

Mineralogy. — “*On an “Eisenrose” of the St. Gotthard.*” By G. B. HOGENRAAD. (Communicated by Prof. J. L. C. SCHROEDER VAN DER KOLK).

Some time ago I tried to get a Hematite-streak with a so-called “Eisenrose.” I did not succeed however, for to my astonishment the streak was not red but black. Several explanations came to my mind:

1^o. that the mineral was somewhat friable, which was the cause that the streak could not consist of the very finest particles. But in rubbing the black colour remained; only the outlines showed a reddish-brown tint. The same was stated with about 25 other pieces of the same finding-place. So that the explanation proved to be not the right one.

2°. that the mineral contained Mn or Ti, since these elements have a great influence on the colour of the streak. But an analysis only produced little Ti and no trace of Mn, so that this explanation did not hold good either.

3°. that the mineral was magnetite. In its favour spoke the very distinct magnetism, stronger than hematite generally shows.

I then consulted some literature, to see whether anything had been written before on the streak, the magnetism and the chemical composition of "Eisenrose."

DANA says ¹⁾ :

St. Gotthard affords beautiful specimens, composed of crystallised tables grouped in the forms of rosettes (Eisenrosen), and accompanying crystals of adularia.

DANA calls this occurring Hematite, though he neither speaks of the chemical composition, nor gives any particulars about streak or magnetism.

In the "Zeitschrift für Krystallographie und Mineralogie von P. GROTH" I found in Number 13 on p. 301 a report by A. CATHREIN from STRÜVER's account on "Pseudomorphose von Magnetit nach Eisenglimmer von Ogliastra in Sardinien", written in the Atti della Reale Accademia Dei Lincei 1886. Volume II, 2°. Semestre, p. 331. The report in question follows here :

„Die Hauptmasse der Stufe besteht aus einem grobkörnigen Mineral, dessen unregelmässigen Individuen von mehreren Centimetern Durchmesser fest mit einander verwachsen erscheinen. Jedes Korn zerfällt nach einer Richtung äusserst leicht in dünnste Lamellen. Härte 6, Pulver schwarz, stark magnetisch, schwer schmelzbar, in Salzsäure leicht löslich. Diese Eigenschaften kommen dem Magnetit zu. Das Gemenge erscheint ganz frisch, unverändert und ursprünglicher Entstehung. Dass es sich hier nicht um nach {111} blätterig abgesonderten Magnetit handelt, folgt aus dem Mangel jeder Spur von Spaltbarkeit nach einer anderen Richtung ausser jener einen. Die Lamellarstructur als Druckwirkung aufzufassen verbietet die Richtungsänderung der Lamellen in jedem einzelnen Korn. Nach des Verfassers Ansicht bleibt nur die Annahme einer Pseudomorphose von Magnetit nach Eisenglimmer.“

So this appearance as regards streak and magnetism corresponds with the specimen examined by me. Through the absence of a chemical analysis it cannot be decided in how far the supposition is right, that he had to do here with a pseudomorphosis from Magnetite to Eisenglimmer.

¹⁾ A System of Mineralogy p. 216.

In the "Zeitschrift der Geologischen Gesellschaft" Bd. 22, 1870 I found on page 719 in an article by G. vom Rath the following statement ¹⁾:

"Pseudomorphische Massen von Magneteisen nach Eisenglanz. Farbe und Strich schwarz, schimmernd auf dem Bruch, magnetisch. Das Erz ist aber weder dicht, noch körnig (wie es sonst dem Magneteisen zukommt), sondern schuppig. Man erkennt sogar in einzelnen Drusen ganz deutlich die hexagonalen Formen des ursprünglichen Eisenglanzes; doch auch diese letzteren haben einen schwarzen Strich. Vermuthlich ist demnach jene ganze colossale Schichtenmasse bei Vallone ursprünglich Eisenglanz gewesen".

So to this can be applied what has been remarked on STRÜVER'S article.

Finally D. F. WISER says ²⁾:

Die Eisen-Rosen vom Pomonetto wirken sehr stark auf die Magnet-Nadel. Das Strich-Pulver ist dunkel-röthlichbraun, beinahe schwarz.

Die Wirkung auf die Magnet-Nadel ist bei den Schweizerischen Eisenglanzen gar sehr verschieden, sowie die Nüanzirungen von Eisen-schwarz bis Stahlgrau in ihrer Färbung. Bemerkenswerth scheint es mir, dass die Eisen-Rosen ohne aufliegende Rutil-Krystalle immer die schwärzeste Farbe zeigen, und dass dieselbe hingehend immer heller wird, je mehr Rutil auf den End-Flächen der Eisenglanz-Tafeln, ich möchte sagen, ausgeschieden worden ist.

Die Mineralien, welche die Eisen-Rosen vom Pomonetto begleiten, sind: kleine, graulich-weiße Adular-Krystalle, kleine sechseckige Tafeln von Tombackbraunen Glimmer und eine schmutzig grünlich-gelbe Rindenformige Substanz die vielleicht den Chloriten beigezählt werden darf.

Mein Freund, Hr Bergrath STOCKAR hieselbst, hat die Eisen-Rose vom Pomonetto analysirt und wird hoffentlich nächstens das Resultat seiner Untersuchungen veröffentlichen."

However I could not find this promised analysis anywhere in literature, so that I decided to do it myself (I). For a good control the same analysis was made by Messrs B. H. VAN DER LINDE (II) and G. W. MALLÉE (III). The results of our investigations were as follows:

¹⁾ Geognostisch-mineralogische Fragmente aus Italiën, chapter VIII: Die Insel Elba, Zeitschr. D. G. G. 1870.

²⁾ Bericht über Mineraliën aus der Schweiz. N. Jahrb. 1854 p. 26.

	I.	II.	III.
Fe	69,94	69,13	69,50
O	29,97	29,60	30,46
accompanying mineral		1,2	
	99,91	99,93	99,96 ¹⁾

Reckoned for :

	Hematite	Magnetite
Fe	70	72,41
O	30	27,59.

So that my conclusion is that we have not to do with Magnetite but with Hematite.

The results of my researches are in consequence the following:

1st. That I have had to do with Hematite with very obvious magnetism and a black streak, which in rubbing along the outlines shows a brown tint (which generally every black streak does) and not with a pseudomorphosis from Magnetite to Hematite.

2nd. That where in literature of this occurrence of Hematite has been spoken, no analysis has been added, though the magnetism and the black streak have been observed more than once.

3rd. That it is desirable to convince oneself of the chemical composition with every "Eisenrose", which shows these characteristics.

Physics. — "*Contributions to the theory of electrons.*" I. By Prof. H. A. LORENTZ.

Simplification of the fundamental equations by the introduction of new units.

§ 1. If all quantities are expressed in electromagnetic units, as I have done in former papers, the relations between the volume-density ρ of the charge of an electron, the velocity v of its points, the

¹⁾ I here by have to mention that first the figure for the oxygen was determined by reduction in a hydrogen-current und weighing of the water absorbed by CaCl_2 ; that after that the figure for the iron was determined by dissolving the reduced mineral in dilute H_2SO_4 and making a titration of this solution (after reduction in a H_2S -current and after removing the H_2S by boiling in a CO_2 atmosphere) with a KMnO_4 -solution, of which 1 cm^3 corresponded with 8,9 m.G. Fe.

The presence of Ti was shown as follows: the mineral was melted together with KHSO_4 , the fused mass dissolved in cold water. This solution together with H_2O_2 gave the well-known orange colour of TiO_3 . Moreover after adding a little HNO_3 , the Ti after having been boiled precipitated as white TiO_2 . The accompanying mineral, which in microscopic examination proved to be adularia, was removed as much as possible.

dielectric displacement \mathfrak{d} in the aether, the current \mathfrak{l} and the magnetic force \mathfrak{h} are as follows ¹⁾:

$$\begin{aligned} \operatorname{div} \mathfrak{d} &= \varrho, \\ \frac{\partial \varrho}{\partial t} + \operatorname{div} (\varrho \mathfrak{v}) &= 0, \\ \mathfrak{l} &= \dot{\mathfrak{d}} + \varrho \mathfrak{v}, \\ \operatorname{div} \mathfrak{h} &= 0, \\ \operatorname{rot} \mathfrak{h} &= 4 \pi \mathfrak{l} = 4 \pi (\dot{\mathfrak{d}} + \varrho \mathfrak{v}), \\ 4 \pi c^2 \operatorname{rot} \mathfrak{d} &= -\dot{\mathfrak{h}}, \end{aligned}$$

where c is the velocity of light in the aether. To these equations we must add the formula

$$\mathfrak{f} = 4 \pi c^2 \mathfrak{d} + [\mathfrak{v} \cdot \mathfrak{h}]$$

for the electric force, i. e. the force, reckoned per unit charge, which the aether exerts on a charged element of volume.

The equations take a somewhat more regular form if we express ϱ , \mathfrak{d} , \mathfrak{l} and \mathfrak{f} in electrostatic units (preserving the electromagnetic unit for \mathfrak{h}) and a further simplification is obtained, if, instead of the units for charge and magnetic pole that are usually taken as the basis of the electrostatic and electromagnetic systems, we choose new ones, $\sqrt{4\pi}$ times smaller ²⁾. Introducing both modifications, we have to replace ϱ , \mathfrak{d} , \mathfrak{l} by $\frac{\varrho}{c\sqrt{4\pi}}$, $\frac{\mathfrak{d}}{c\sqrt{4\pi}}$, $\frac{\mathfrak{l}}{c\sqrt{4\pi}}$, \mathfrak{f} by $c\sqrt{4\pi} \cdot \mathfrak{f}$, because this letter must now represent the force acting on the new unit of charge, and likewise \mathfrak{h} by $\sqrt{4\pi} \cdot \mathfrak{h}$.

This leads to the equations

$$\operatorname{div} \mathfrak{d} = \varrho, \dots \dots \dots \quad (\text{I})$$

$$\frac{\partial \varrho}{\partial t} + \operatorname{div} (\varrho \mathfrak{v}) = 0, \dots \dots \dots \quad (\text{II})$$

$$\mathfrak{l} = \dot{\mathfrak{d}} + \varrho \mathfrak{v}, \dots \dots \dots \quad (\text{III})$$

$$\operatorname{div} \mathfrak{h} = 0, \dots \dots \dots \quad (\text{IV})$$

$$\operatorname{rot} \mathfrak{h} = \frac{1}{c} \mathfrak{l} = \frac{1}{c} (\dot{\mathfrak{d}} + \varrho \mathfrak{v}), \dots \dots \dots \quad (\text{V})$$

¹⁾ See my *Versuch einer Theorie der electrischen und optischen Erscheinungen in bewegten Körpern*. I shall again suppose that all quantities are continuous functions of the coordinates, so that e.g. the density ρ will be regarded as passing gradually to the value 0, which it has outside an electron. With the exception of the letters, the notations are the same as in the just mentioned treatise. The scalar product of two vectors \mathfrak{a} and \mathfrak{b} will be denoted by $(\mathfrak{a} \cdot \mathfrak{b})$, the vector product by $[\mathfrak{a} \cdot \mathfrak{b}]$. The axes of coordinates are supposed to remain at rest, relatively to the aether.

²⁾ This change has been warmly advocated by HEAVISIDE. The units I shall now use are those that have been adopted for the *Mathematische Encyclopädie*.

$$\text{rot } \mathbf{d} = -\frac{1}{c} \dot{\mathbf{h}}, \dots \dots \dots \text{ (VI)}$$

$$\mathbf{f} = \mathbf{d} + \frac{1}{c} [\mathbf{v} \cdot \mathbf{h}]. \dots \dots \dots \text{ (VII)}$$

In connexion with the last formula it may be remarked that \mathbf{d} is the electric force that would act on an immovable charge.

The electric energy per unit-volume is given by

$$W_e = \frac{1}{2} \mathbf{d}^2, \dots \dots \dots \text{ (VIII)}$$

the magnetic energy per unit-volume by

$$W_m = \frac{1}{2} \mathbf{h}^2, \dots \dots \dots \text{ (IX)}$$

and POYNTING'S flux of energy by

$$\mathfrak{E} = c [\mathbf{d} \cdot \mathbf{h}]. \dots \dots \dots \text{ (X)}$$

We shall further write U for the total electric and T for the total magnetic energy of a system.

The equations, (IV) and (V) suffice for the determination of the magnetic force \mathbf{h} , as soon as the current \mathbf{l} is given in every point. W_m is then known by (IX) and T follows by integration. In this sense, every motion of electricity may be said to be accompanied by a definite amount of magnetic energy.

Scalar potential and vector-potential.

§ 2. The equations of § 1 apply to every system in which charged matter moves through the aether, whether the charge be confined to certain extremely small parts of space (electrons) or otherwise distributed. Moreover, the motions may be of any kind; the electrons may have a pure translatory motion, or a rotation at the same time, and we may even suppose their form to change in the course of time. For the validity of the formulae it is however required that each element of volume whose points move with the charged matter should preserve its charge, though its form and dimensions may change. This is expressed by the equation (II) and it is on this ground that the electric current \mathbf{l} , as defined by (III), (the resultant of the displacement-current $\dot{\mathbf{d}}$ and the convection-current \mathbf{qv}) may always be said to be solenoidally distributed, so that

$$\text{div } \mathbf{l} = 0.$$

If now the motion of the charged matter is given, the electromagnetic field in the aether, within and without that matter, has

to be determined by means of (I)—(VI), a problem that may be reduced to equations of the form

$$\Delta\psi - \frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2} = -\alpha, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which α is a known, and ψ an unknown function of x, y, z, t .

Let σ be any closed surface and n the normal to it, drawn outwards.

Then, if the equation (1) holds in the whole space S , enclosed by σ , we shall have for the value of ψ in a point P of this space, at the time t ,

$$\psi = \frac{1}{4\pi} \int \frac{1}{r} [\alpha] dS + \frac{1}{4\pi} \int \left\{ \frac{1}{r} \left[\frac{\partial \psi}{\partial n} \right] - [\psi] \frac{\partial}{\partial n} \left(\frac{1}{r} \right) \right\} d\sigma. \quad . \quad . \quad (2)$$

Here the first integral extends over the space S and the second over the boundary surface σ ; r is the distance to P , and the square brackets serve to indicate the values of the enclosed quantities for the time $t - \frac{r}{c}$.

Let us now conceive the surface σ to recede on all sides to infinite distance and let the circumstances be such that the surface-integral in (2) has the limit 0. Then, ultimately:

$$\psi = \frac{1}{4\pi} \int \frac{1}{r} [\alpha] dS, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where the integration must be extended over infinite space.

§ 3. Equations of the form (1) may be deduced from the formulae (I)—(VI) in many different ways; they may e.g. be established for each of the components of \mathfrak{d} and \mathfrak{b} .¹⁾ The solution is however obtained in a simpler form²⁾, if one introduces four auxiliary quantities, a scalar potential φ and the three components $\mathfrak{a}_x, \mathfrak{a}_y, \mathfrak{a}_z$ of a vector-potential \mathfrak{a} . These quantities satisfy the equations

$$\Delta\varphi - \frac{1}{c^2} \frac{\partial^2 \varphi}{\partial t^2} = -\varrho.$$

$$\Delta \mathfrak{a}_x - \frac{1}{c^2} \frac{\partial^2 \mathfrak{a}_x}{\partial t^2} = -\frac{1}{c} \varrho v_x, \quad \Delta \mathfrak{a}_y - \frac{1}{c^2} \frac{\partial^2 \mathfrak{a}_y}{\partial t^2} = -\frac{1}{c} \varrho v_y, \quad \text{etc.},$$

so that, with the restrictions that are required if (3) is to be true, we may write

$$\varphi = \frac{1}{4\pi} \int \frac{1}{r} [\varrho] dS,$$

¹⁾ LORENTZ, La théorie électromagnétique de MAXWELL et son application aux corps mouvants, Arch. néerl. T. 25, p. 476 1892.

²⁾ See LEVI CIVITA, Nuovo Cimento, (4), vol. 6, p. 93, 1897; WIECHERT, Arch. néerl., (2), T. 5, p. 549, 1900.

$$a_x = \frac{1}{4\pi c} \int \frac{1}{r} [q v_x] dS \quad , \quad a_y = \frac{1}{4\pi c} \int \frac{1}{r} [q v_y] dS, \text{ etc.}$$

After having found φ and \mathbf{a} , we may determine the dielectric displacement \mathbf{d} and the magnetic force \mathbf{h} by means of the relations ¹⁾

$$\mathbf{d} = -\frac{1}{c} \dot{\mathbf{a}} - \text{grad } \varphi, \dots \dots \dots (4)$$

$$\mathbf{h} = \text{rot } \mathbf{a}. \dots \dots \dots (5)$$

It is to be remarked that the two potentials are not mutually independent; they are connected by the equation

$$\text{div } \mathbf{a} = -\frac{1}{c} \dot{\varphi}. \dots \dots \dots (6)$$

Theorems corresponding to the principle of D'ALEMBERT and that of least action.

§ 4. The physicists who have endeavoured, by means of certain hypotheses on the mechanism of electromagnetic phenomena, to deduce the fundamental equations from the principles of dynamics, have encountered considerable difficulties, and it is best, perhaps, to leave this course, and to adopt the equations (I)—(VII) — or others, equivalent to them — as the simplest expression we may find for the laws of electromagnetism. Nevertheless, even if we prefer this point of view, it deserves notice that the fundamental equations may be transformed in such a way that we arrive at theorems of the same mathematical form as the general principles of dynamics. This has been done especially by ABRAHAM in his important paper “Principien der Dynamik des Elektrons”²⁾. The considerations in this and the two next paragraphs agree with those of ABRAHAM, though presented in a form differing from his.

We shall consider a system of electrons moving in the infinitely extended aether, and we shall fix our attention on the different states of this system, the aether included, that succeed each other in the course of time in any electromagnetic phenomenon. From every one of these states we shall pass to another, differing infinitely little from it, and which we shall call the *varied* state. The variation or “virtual change” will consist in infinitely small displacements \mathfrak{q} of

¹⁾ I shall write *grad* φ („gradient of φ ”) for the vector whose components are $\frac{\partial \varphi}{\partial x}, \frac{\partial \varphi}{\partial y}, \frac{\partial \varphi}{\partial z}$.

²⁾ DRUDE'S *Annalen*, 10, p. 105, 1903.

the points of the electrons, accompanied by infinitesimal changes in the dielectric displacement.

We shall write $\delta\mathfrak{d}$ for the difference, in a fixed point of the aether, between the dielectric displacement before and after the virtual change, the sign of variation δ having a similar meaning when it precedes other symbols representing the value of some quantity in a definite point. If it is affixed to a letter representing a quantity belonging to the system as a whole, such as the total electric energy U , it will simply serve to indicate the difference between these values in the original or real and the varied states.

The variations to be considered are not wholly arbitrary. We shall limit our choice by supposing in the first place that each element of volume of an electron preserves its charge during the displacements \mathfrak{q} ; this is expressed by the relation

$$\delta\mathfrak{q} + \text{div}(\mathfrak{q}\mathfrak{q}) = 0, \dots\dots\dots (7)$$

which may be compared to (II).

In the second place we shall suppose the variations of \mathfrak{d} not to violate the condition (I).

In virtue of these restrictions the vector

$$\delta\mathfrak{d} + \mathfrak{q}\mathfrak{q}$$

will present a solenoidal distribution. Indeed, we see from (I) that

$$\text{div}\delta\mathfrak{d} = \delta\mathfrak{q},$$

and here we may, according to (7), replace the right-hand member by $-\text{div}(\mathfrak{q}\mathfrak{q})$.

Let us now conceive \mathfrak{q} and $\delta\mathfrak{d}$ to be chosen for every instant t , so that they vary continuously with the time. Then, in order completely to define the succession of varied states, or what we may call the "varied motion" of the system, we shall suppose the varied positions of the points of each electron to be reached at the same instants at which these points occupy the corresponding original positions in the real motion; we assume likewise that, in every point of space, the varied dielectric displacement exists at the same moments as the original one in the succession of real states.

By this the varied motion of electricity is entirely determined; indeed, since we know the velocity of matter and the rate at which \mathfrak{d} changes, we are able to state what has become of the convection-current, the displacement-current, and also of the total current I . The first thing we have to do will be to express δI in \mathfrak{q} and $\delta\mathfrak{d}$. Of course we may be sure beforehand that the distribution of both the new I and the variation δI will be solenoidal. This must necessarily be the case, because we know 1st. that, in the states that succeed one another in the varied motion, each volume-element of

an electron retains its charge, and 2nd. that the condition (I) is continually fulfilled.

§ 5. Let us begin by considering $\delta \mathbf{v}_x$. This is the variation in a fixed point of space. Therefore, if $(\delta \mathbf{v}_x)$ is the variation for a definite point of an electron, we shall have

$$(\delta \mathbf{v}_x) = \delta \mathbf{v}_x + q_x \frac{\partial \mathbf{v}_x}{\partial x} + q_y \frac{\partial \mathbf{v}_x}{\partial y} + q_z \frac{\partial \mathbf{v}_x}{\partial z}.$$

As to $(\delta \mathbf{v}_x)$, it is easily shown to have the value

$$(\delta \mathbf{v}_x) = \frac{d\mathfrak{q}_x}{dt},$$

if we understand by $\frac{d\mathfrak{q}_x}{dt}$ the rate at which \mathfrak{q}_x changes for a definite point of an electron. Comparing this to $\frac{\partial \mathfrak{q}_x}{\partial t}$ or $\dot{\mathfrak{q}}_x$, the velocity of change in a fixed point of space, we get

$$(\delta \mathbf{v}_x) = \dot{\mathfrak{q}}_x + \mathbf{v}_x \frac{\partial \mathfrak{q}_x}{\partial x} + \mathbf{v}_y \frac{\partial \mathfrak{q}_x}{\partial y} + \mathbf{v}_z \frac{\partial \mathfrak{q}_x}{\partial z}.$$

These equations, combined with (7), lead us to

$$\begin{aligned} \delta l_x &= \delta (\dot{\mathbf{v}}_x + \rho \mathbf{v}_x) = \delta \dot{\mathbf{v}}_x + \rho \delta \mathbf{v}_x + \mathbf{v}_x \delta \rho = \\ &= \delta \dot{\mathbf{v}}_x + \rho \dot{\mathfrak{q}}_x + \rho \mathbf{v}_x \frac{\partial \mathfrak{q}_x}{\partial x} + \rho \mathbf{v}_y \frac{\partial \mathfrak{q}_x}{\partial y} + \rho \mathbf{v}_z \frac{\partial \mathfrak{q}_x}{\partial z} - \\ &- \rho q_x \frac{\partial \mathbf{v}_x}{\partial x} - \rho q_y \frac{\partial \mathbf{v}_x}{\partial y} - \rho q_z \frac{\partial \mathbf{v}_x}{\partial z} - \mathbf{v}_x \operatorname{div}(\rho \mathfrak{q}), \end{aligned}$$

or, if we add to the second member the first member of (II), multiplied by q_x , after some further transformation,

$$\begin{aligned} \delta l_x &= \frac{\partial}{\partial t} (\delta \mathbf{v}_x + \rho \mathfrak{q}_x) + \rho \mathbf{v}_x \frac{\partial \mathfrak{q}_x}{\partial x} + \rho \mathbf{v}_y \frac{\partial \mathfrak{q}_x}{\partial y} + \rho \mathbf{v}_z \frac{\partial \mathfrak{q}_x}{\partial z} - \mathbf{v}_x \operatorname{div}(\rho \mathfrak{q}) - \\ &- \rho q_x \frac{\partial \mathbf{v}_x}{\partial x} - \rho q_y \frac{\partial \mathbf{v}_x}{\partial y} - \rho q_z \frac{\partial \mathbf{v}_x}{\partial z} + q_x \operatorname{div}(\rho \mathbf{v}) = \\ &= \frac{\partial}{\partial t} (\delta \mathbf{v}_x + \rho \mathfrak{q}_x) + \frac{\partial}{\partial y} [\rho (q_x \mathbf{v}_y - q_y \mathbf{v}_x)] - \frac{\partial}{\partial z} [\rho (q_x \mathbf{v}_z - q_z \mathbf{v}_x)]. \end{aligned}$$

Here we may remark that the two last terms taken together represent the first component of the "rotation" of the vector whose components are

$$\rho (q_y \mathbf{v}_z - q_z \mathbf{v}_y), \rho (q_z \mathbf{v}_x - q_x \mathbf{v}_z), \rho (q_x \mathbf{v}_y - q_y \mathbf{v}_x),$$

and that this vector is precisely the vector-product, multiplied by ρ , of \mathfrak{q} and \mathbf{v} . After having calculated δl_y and δl_z in the same way as δl_x , we may combine the results in the formula

$$\sigma l = \frac{\partial}{\partial t} (\sigma \mathfrak{d} + \mathfrak{q} \mathfrak{q}) + \text{rot} \{ \mathfrak{q} [\mathfrak{q} \cdot \mathfrak{v}] \} \dots \dots \dots (8)$$

What has already been said about the solenoidal distribution of σl is confirmed by this equation. The two vectors represented on the right hand side both have this property, the first by what we know of the vector $\sigma \mathfrak{d} + \mathfrak{q} \mathfrak{q}$, and the second on account of the mathematical form in which it appears.

§ 6. We may next proceed to determine the variation σT of the magnetic energy. In doing so we shall start from the assumption that the varied motion of electricity involves a definite magnetic energy ¹⁾, to be determined as stated at the end of § 1.

The formula

$$T = \frac{1}{2} \int \mathfrak{b}^2 dS$$

leads immediately to

$$\sigma T = \int (\mathfrak{b}_x \sigma \mathfrak{b}_x + \mathfrak{b}_y \sigma \mathfrak{b}_y + \mathfrak{b}_z \sigma \mathfrak{b}_z) dS = \int (\mathfrak{b} \cdot \sigma \mathfrak{b}) dS,$$

where the integration covers all space. The same will be the case with the other volume-integrals appearing in the following transformations. If an integration is performed, or if the process of integration by parts is applied, one obtains integrals over the infinite surface which we may conceive as the boundary of the field of integration. These surface-integrals however will be supposed to vanish.

We begin by writing $\text{rot } \mathfrak{a}$ instead of \mathfrak{b} , as may be done in virtue of (5); and we shall next integrate by parts, keeping in mind that, on account of (V),

$$\text{rot } \sigma \mathfrak{b} = \frac{1}{c} \cdot \sigma l.$$

The result is

$$\sigma T = \int (\text{rot } \mathfrak{a} \cdot \sigma \mathfrak{b}) dS = \int (\mathfrak{a} \cdot \text{rot } \sigma \mathfrak{b}) dS = \frac{1}{c} \int (\mathfrak{a} \cdot \sigma l) dS, \dots (9)$$

or, if we substitute for σl its value (8),

$$\sigma T = \frac{1}{c} \int \left(\mathfrak{a} \cdot \frac{\partial}{\partial t} \{ \sigma \mathfrak{d} + \mathfrak{q} \mathfrak{q} \} \right) dS + \frac{1}{c} \int \left(\mathfrak{a} \cdot \text{rot} \{ \mathfrak{q} [\mathfrak{q} \cdot \mathfrak{v}] \} \right) dS. (10)$$

Using (4), we may put for the first term

¹⁾ This assumption only means to define the value of T we shall assign to the wholly fictitious varied state.

$$\frac{1}{c} \frac{d}{dt} \int (\mathbf{a} \cdot \{\sigma \mathbf{d} + \rho \mathbf{q}\}) dS - \frac{1}{c} \int (\dot{\mathbf{a}} \cdot \{\sigma \mathbf{d} + \rho \mathbf{q}\}) dS =$$

$$= \frac{1}{c} \frac{d}{dt} \int (\mathbf{a} \cdot \{\sigma \mathbf{d} + \rho \mathbf{q}\}) dS + \int (\mathbf{b} \cdot \{\sigma \mathbf{d} + \rho \mathbf{q}\}) dS + \int (\text{grad } \varphi \cdot \{\sigma \mathbf{d} + \rho \mathbf{q}\}) dS. \quad (11)$$

Now, it appears from (9) that

$$\frac{1}{c} \int (\mathbf{a} \cdot \{\sigma \mathbf{d} + \rho \mathbf{q}\}) dS (12)$$

is the change the magnetic energy of the system would undergo, if we gave to the current the change $\sigma \mathbf{d} + \rho \mathbf{q}$. We shall write $\sigma' l$ for *this* variation of the current, and $\sigma' h$, $\sigma' T$ for the corresponding variations of h and T . As to $\sigma' l$, it may be defined as the current that would exist if the changes represented by \mathbf{q} and $\sigma \mathbf{d}$ were accomplished in unit of time.

On the other hand, $\int (\mathbf{b} \cdot \sigma \mathbf{d}) dS$ is the variation of the electric energy U and the last integral in (11) is 0, because the vector $\sigma \mathbf{d} + \rho \mathbf{q}$ is solenoidally distributed. Thus, the first term in (10) becomes

$$\frac{d\sigma' T}{dt} + \sigma U + \int (\mathbf{b} \cdot \rho \mathbf{q}) dS.$$

For the last term in that equation we find, integrating by parts,

$$\frac{1}{c} \int (\text{rot } \mathbf{a} \cdot \{\rho [\mathbf{q} \cdot \mathbf{v}]\}) dS = \frac{1}{c} \int \rho (\mathbf{b} \cdot [\mathbf{q} \cdot \mathbf{v}]) dS = \frac{1}{c} \int \rho (\mathbf{q} \cdot [\mathbf{v} \cdot \mathbf{b}]) dS,$$

so that finally

$$\sigma T = \frac{d\sigma' T}{dt} + \sigma U + \int \rho \left(\mathbf{q} \cdot \left\{ \mathbf{d} + \frac{1}{c} [\mathbf{v} \cdot \mathbf{b}] \right\} \right) dS.$$

Now, the equation (VII) shows that the last term is precisely the work done, during the displacements \mathbf{q} , by the electric forces exerted by the aether on the electrons.

Writing σE for this work, we have

$$\sigma E = \sigma (T - U) - \frac{d\sigma' T}{dt} (13)$$

an equation closely corresponding to D'ALEMBERT's principle in common dynamics.

§ 7. The motion of the electrons themselves may be determined by ordinary methods; it will be governed by the electric forces whose work has been denoted by σE , together with forces of any other kind that may come into play. We shall confine ourselves to those cases in which these latter forces depend on a potential energy U_1 ; then the total virtual work of all forces acting on the

electrons will be $\delta E - \delta U_1$. Moreover we shall ascribe to the electrons a certain kinetic energy T_1 , which they have by virtue of their mass in the ordinary sense of the word. Should there be no such "true" mass, we have only to put $T_1 = 0$.

One of the forms that may be given to the variational equation of motion for a system of material particles is

$$\delta A = \frac{d\delta' T_1}{dt} - \delta T_1,$$

δT_1 being the change of T_1 , if we pass from the real motion to some varied motion in which the varied positions are reached at the same moments as the original positions in the real motion, δA the virtual work of the forces, and $\delta' T_1$ the increment that would be acquired by the kinetic energy T_1 , if variations, equal to the virtual changes of the coordinates, were imparted to the corresponding velocities (the coordinates themselves being kept constant). For our system of electrons

$$\delta A = \delta E - \delta U_1;$$

hence, if we use for δE the formula (13),

$$\delta \{ (T + T_1) - (U + U_1) \} - \frac{d\delta'(T + T_1)}{dt} = 0.$$

We shall finally multiply this by dt and integrate from t_1 to t_2 . In case both the displacements \mathfrak{q} and the variations $\delta \mathfrak{d}$ vanish at the limits, we find

$$\delta \int_{t_1}^{t_2} \{ (T + T_1) - (U + U_1) \} dt = 0.$$

This is analogous to the principle of least action.

§ 8. In what precedes there has been question of the variations of the energies T and U , taken for the system of electrons together with the surrounding aether, which extends to infinite distance. Similar though somewhat less simple results are obtained, if one understands by T and U the magnetic and the electric energies, in so far only as they belong to the space within an immovable closed surface σ . In what follows it is to be understood that this surface may have, relatively to the system of electrons, any position we like; for simplicity's sake however we shall suppose that it cuts none of them, so that, in every point of σ , the density $\rho = 0$. As to the virtual variations, determined by \mathfrak{q} and $\delta \mathfrak{d}$, they need not at all be confined to the part of the system within the surface. We shall denote by n the normal to the surface, drawn towards the

outside, and by λ, μ, ν the angles between this normal and the positive axes of coordinates.

If now we repeat the above calculations, we have to do with volume-integrals confined to the space within σ , and every integration by parts will give rise to a surface-integral.

Thus, to the last member of (9) we shall have to add the term

$$\int \begin{vmatrix} \cos \lambda, \cos \mu, \cos \nu \\ a_x, a_y, a_z \\ \delta b_x, \delta b_y, \delta b_z \end{vmatrix} d\sigma = \int [\mathbf{a} \cdot \delta \mathbf{b}]_n d\sigma$$

and the value of (12) will no longer be $\delta' T$, but

$$\delta' T - \int \begin{vmatrix} \cos \lambda, \cos \mu, \cos \nu \\ a_x, a_y, a_z \\ \delta' b_x, \delta' b_y, \delta' b_z \end{vmatrix} d\sigma = \delta' T - \int [\mathbf{a} \cdot \delta' \mathbf{b}]_n d\sigma. \quad (14)$$

The last integral of (11) becomes

$$c \int (\text{grad } \varphi \cdot \text{rot } \delta' \mathbf{b}) dS = c \int (\text{rot grad } \varphi \cdot \delta' \mathbf{b}) dS - c \int [\text{grad } \varphi \cdot \delta' \mathbf{b}]_n d\sigma \quad (15)$$

Here the first term on the right-hand side is 0, since $\text{rot grad } \varphi = 0$. The transformation of the last part of (10) remaining as it was, as we have supposed $\varphi = 0$ in all points of the surface, we finally find for the second member of (13) the additional term

$$\int \left\{ -[\mathbf{a} \cdot \delta \mathbf{b}]_n + \frac{\partial}{\partial t} [\mathbf{a} \cdot \delta' \mathbf{b}]_n + c [\text{grad } \varphi \cdot \delta' \mathbf{b}]_n \right\} d\sigma.$$

But, on account of (4),

$$\begin{aligned} & \frac{\partial}{\partial t} [\mathbf{a} \cdot \delta' \mathbf{b}]_n + c [\text{grad } \varphi \cdot \delta' \mathbf{b}]_n = \\ & = \left[\mathbf{a} \cdot \left\{ \frac{\partial \delta' \mathbf{b}}{\partial t} \right\} \right]_n + [\dot{\mathbf{a}} \cdot \delta' \mathbf{b}]_n + c [\text{grad } \varphi \cdot \delta' \mathbf{b}]_n = \\ & = \left[\mathbf{a} \cdot \left\{ \frac{\partial \delta' \mathbf{b}}{\partial t} \right\} \right]_n - c [\mathfrak{D} \cdot \delta' \mathbf{b}]_n, \end{aligned}$$

We get therefore, instead of (13),

$$\delta E = \delta(T - U) - \frac{d\delta' T}{dt} + \int \left\{ \left[\mathbf{a} \cdot \left\{ \frac{\partial \delta' \mathbf{b}}{\partial t} \right\} - \delta \mathbf{b} \right]_n - c [\mathfrak{D} \cdot \delta' \mathbf{b}]_n \right\} d\sigma \quad (16)$$

§ 9. The following are some examples of the applications that may be made of the formulae (13) and (16).

a. Let the virtual changes in the position of the electrons and in the dielectric displacement be proportional to the rates of change in the real motion, i. e. let

$$\delta \mathbf{r} = \varepsilon \mathbf{v}, \quad \delta \mathfrak{D} = \varepsilon \dot{\mathfrak{D}},$$

ε being a constant infinitely small factor. From these assumptions it follows at once that

$$\delta' t = \varepsilon t, \quad \delta' \mathfrak{h} = \varepsilon \mathfrak{h}.$$

Now the magnetic energy may be considered as a homogeneous quadratic function of the components of the current; it will therefore change in ratio of 1 to $1 + 2\varepsilon$, if the current becomes $(1 + \varepsilon)I$. Thus: $\delta' T = 2\varepsilon T$.

We may also infer from our assumptions that the position of the electrons and the values of \mathfrak{d} are, in the varied motion at the time t , what they are in the real motion at the time $t + \varepsilon$, so that the only difference between the two motions is that the one is in advance of the other by an interval ε .

In this way it is seen that

$$\delta T = \varepsilon \frac{dT}{dt}, \quad \delta U = \varepsilon \frac{dU}{dt}, \quad \delta \mathfrak{h} = \varepsilon \frac{\partial \mathfrak{h}}{\partial t}, \quad \frac{\partial \delta' \mathfrak{h}}{\partial t} - \delta \mathfrak{h} = 0.$$

Substituting these values in the equation (16), we get, after division by ε and multiplication by dt , denoting by dE the work done by the electric forces in the real motion, during the time dt ,

$$dE = -d(T + U) - c dt \int [\mathfrak{d} \cdot \mathfrak{h}]_n d\sigma. \quad \dots \quad (17)$$

This is the equation of energy. The last term represents the flow of energy through the surface.

b. Applying (17) to a single electron, whose motion is a translation with variable velocity along a straight line, one may calculate the force with which it is acted on by the aether, and which, under certain simplifying assumptions, is found to be proportional to the acceleration and directed oppositely to it. The quotient of this force, divided by the acceleration, may appropriately be called the *electromagnetic mass* of the electron.

c. There will likewise be a force proportional and opposed to the acceleration, if the latter is perpendicular to the direction of motion. In this case however, of which the uniform motion of an electron in a circle furnishes the simplest example, we must recur to the equation (16), in order to determine the force. The surface σ may be supposed to lie at infinite distance and the virtual displacement must be taken in the direction of the acceleration. The ratio of the force and the acceleration may again be called the *electromagnetic mass*, though, except for small velocities, its value is not equal to that of the corresponding ratio in the case *b*.

In both cases the result agrees with what has been found by ABRAHAM.

Ponderomotive action on a system of electrons.

§ 10. A virtual change of a very simple kind is an infinitely small translation of all the electrons, combined with what we may call an equal translation in the same direction of the whole electric field. Applying to these variations — which we give as well to the part of the system outside the surface σ as to the part enclosed by it — the equation (16), one may calculate the resulting force exerted by the aether on the electrons within the surface. This force may be shown to consist of two parts, the first of which is the force with which we should have to do, if the surface σ were subjected to the stresses in the aether, whose components have been already determined by MAXWELL, whereas the second part is determined by the rate of change of a certain integral, relating to the space S within σ . The latter part will therefore vanish if the state is stationary, and may be left out of account if, for periodic states, we wish only to know the mean value of the resulting force, taken for a full period. I need not here work out the formulae, having formerly deduced the result in a more direct way. The components of MAXWELL's stress are

$$\left. \begin{aligned} X_x &= \frac{1}{2} (d_x^2 - d_y^2 - d_z^2) + \frac{1}{2} (v_x^2 - v_y^2 - v_z^2), \text{ etc.} \\ X_y &= Y_x = d_x d_y + v_x v_y, \text{ etc.} \end{aligned} \right\} \quad (18)$$

and the just mentioned volume-integral is

$$-\frac{1}{c^2} \int \mathfrak{E}_h dS,$$

\mathfrak{E}_h being the flux of energy in the direction h , for which we seek the resulting force.

Thus, the resulting force in the direction of x is given by

$$\Xi = \int X_x d\sigma - \frac{1}{c^2} \frac{d}{dt} \int \mathfrak{E}_x dS. \quad \dots \quad (19)$$

The vector $\frac{1}{c^2} \int \mathfrak{E} dS$ is called by ABRAHAM the *electromagnetic momentum*.

§ 11. Similar results would be obtained if we chose for the virtual variation, instead of a translation, an infinitely small rotation about an axis passing through the origin of coordinates; the equation (16) would then serve to determine the resulting couple, arising from all the forces exerted by the aether on the electrons within the surface σ . The moment of this couple may however be calculated

in a shorter way, if we start from what we know already about the forces.

Indeed, in virtue of the formula (19) and the two corresponding to it, the components of the force acting on an element of volume dS may be represented as follows :

$$\left. \begin{aligned} X dS &= \left(\frac{\partial X_x}{\partial v} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} \right) dS - \frac{1}{c^2} \dot{\mathfrak{E}}_x dS, \\ Y dS &= \left(\frac{\partial Y_x}{\partial v} + \frac{\partial Y_y}{\partial y} + \frac{\partial Y_z}{\partial z} \right) dS - \frac{1}{c^2} \dot{\mathfrak{E}}_y dS, \\ Z dS &= \left(\frac{\partial Z_x}{\partial v} + \frac{\partial Z_y}{\partial y} + \frac{\partial Z_z}{\partial z} \right) dS - \frac{1}{c^2} \dot{\mathfrak{E}}_z dS \end{aligned} \right\} \dots (20)$$

and these formulæ give immediately for the components of the couple

$$\int (yZ - zY) dS = \int (yZ_n - zY_n) d\sigma - \frac{1}{c^2} \int (y\dot{\mathfrak{E}}_z - z\dot{\mathfrak{E}}_y) dS. \quad (21)$$

§ 12. Another consequence of the equations (20), analogous to the well known virial-theorem in ordinary kinetic theory, will perhaps be thought of some interest. In order to find it, we have only to add the three equations, multiplied by x, y, z , and to integrate the result over the space S , within the surface σ . Transforming such terms as $\int x \frac{\partial X_x}{\partial v} dS$ by means of partial integration, we find

$$\begin{aligned} \int (Xx + Yy + Zz) dS &= \int (X_n x + Y_n y + Z_n z) d\sigma - \\ &- \int (X_x + Y_y + Z_z) dS - \frac{1}{c^2} \frac{d}{dt} \int (\mathfrak{E}_x x + \mathfrak{E}_y y + \mathfrak{E}_z z) dS. \quad (22) \end{aligned}$$

For stationary states the last term will vanish, so that, if we substitute in the term preceding it the values (18),

$$\int (Xx + Yy + Zz) dS = \int (X_n x + Y_n y + Z_n z) d\sigma + T + U.$$

Particular cases of ponderomotive action.

§ 13. In a large variety of cases, in which the system of electrons is confined to a space of finite dimensions, the electric and magnetic intensities in the surrounding field become so feeble at great distances that the surface-integrals in (19) and (21) approach the limit 0, if the surface σ moves to infinite distance. Moreover, the volume-integrals will vanish if the state is stationary. We then come to

the conclusion that the resulting force and the resulting couple are 0 for the whole system. If the system consists of two parts A and B , we may express the same thing by saying that the total ponderomotive action on one of these is equal and opposite to the total action on the other.

Of course this will be equally true if, for a system whose state changes periodically, we have only in view the mean ponderomotive action during a full period.

These theorems are useful whenever the phenomena in one of the parts, say in A , are not well enough known to permit a direct calculation of the force acting on this part of the system. If the phenomena in B are less complicated, so that we encounter no difficulty in determining the force or the couple acting on this part, the action on A will be found at the same time.

We may apply this in the first place to well-known experiments on electromagnetic rotations.

Let us consider a cylindrical magnet, touched in two points of its surface by the ends of a conducting wire W . Let this wire be the seat of an electromotive force, producing a current that flows through W and through part of the magnet. The ponderomotive forces acting on the wire are known with certainty and may easily be deduced from the formula (VII); they produce a couple, tending to turn the wire about the axis of the magnet. Without entering into any speculations concerning the motion of the electrons in its interior; we may infer that the magnet will be acted on by an equal couple in the opposite direction.

Of course this reasoning must be justified by showing that the surface-integral in (21) is really 0, if it is taken for a surface at infinite distance. This is readily seen to be the case, if we keep in mind that, at great distances, the magnetic force produced by the system varies inversely as the third power of the distance, and that the intensity of the electric field, if it exist at all, will certainly contain no terms diminishing more slowly than the square of the distance.

§ 14. I shall choose as a second example some experiments, lately made by WHITEHEAD¹⁾ for the purpose of testing a consequence of MAXWELL'S theory that has been admitted by many physicists and is unavoidable in the theory of electrons, viz. that a ponderable dielectric, which is the seat of a variable dielectric displacement, and therefore of a displacement-current, when placed in a magnetic

¹⁾ WHITEHEAD, Ueber die magnetische Wirkung elektrischer Verschiebung, Physikalische Zeitschr., 4, p. 229, 1903.

field, will be acted on by a similar force as a body carrying a conduction-current. In WHITEHEAD'S apparatus two cylindric metallic plates, having the same vertical axis PQ , formed a condenser, in which a rapidly alternating electric field was maintained; at the same time alternating currents were passed through the horizontal windings of a circular coil, surrounding the condenser; the axis of the coil, which is at the same time the axis of its magnetic field, coincided with PQ . A sensitive torsion-balance was suspended by a wire passing along the axis of the instrument; the ends of the beam carried each a piece of some solid dielectric, so that these two equal pieces hung, diametrically opposite each other, in the air-space between the condenser-plates. The two fields, the electric and the magnetic, had exactly the same period, being produced by the same alternate current-machine; besides, the arrangements were such that there was a phase-difference of a quarter period between the two fields. Thus, at the instants at which the magnetic force had its maximum values, the rate of change of the electric field and consequently the intensity of the displacement-current was likewise at its maximum. Under these circumstances a sensible couple acting on the dielectric was expected, but no deviation of the beam, attributable to such a couple, could with certainty be observed.

We may remark in the first place that in WHITEHEAD'S formula for the expected effect, the specific inductive capacity K appears in the numerator. If this were right, a couple would act on the aether between the plates itself. According to the theory of electrons, as here presented, ponderomotive force acts only on the electrons contained in ponderable bodies, but in no case on the aether. The theory therefore regards every ponderomotive action as due to the *difference* between the properties of the body acted upon and the aether; it can lead to a formula containing in the numerator $K-1$, but never to one, containing, instead of this factor, the coefficient K itself.

In the second place WHITEHEAD has overlooked a circumstance by which the effect he sought for must have been, at least for the greater part, compensated. The compensation may be shown to be complete if the properties of the dielectric used differ from those of the aether to so small extent, that quantities which are in this respect of the second order of magnitude, i. e. of the order $(K-1)^2$, may be neglected.

If this may be done, the ponderomotive action on a ponderable dielectric, placed between the condenser-plates, may be considered not to be altered by the presence in the field of a second or third piece of the same dielectric. Now, the two bodies suspended at the ends of WHITEHEAD'S torsion-balance may be taken to have been parts of a

complete dielectric ring, bounded by a surface of revolution with the axis PQ . Moreover it will be safe to assume that the action on the two bodies which it was sought to observe, did not depend on their relative positions with respect to the wires leading to the condenser-plates, and remained therefore the same, in whatever position the torsion-balance was turned. If this was the case, the action on a body that is the n^{th} part of the ring (being cut out of it by two planes passing through the axis) must have been the n^{th} part of the couple, acting on the complete ring. Consequently, it will suffice to show that the effect is 0, if the experiment is made with a complete dielectric ring.

§ 15. For simplicity's sake we shall suppose the condenser-plates to be united by a wire W and their alternating electric charges to be produced by a periodic electromotive force in this wire. As to the currents in the coil, they may be regarded as due to electromotive forces of the same period, acting in the windings themselves; indeed, the action on the dielectrics can only depend on the magnetic field and not on the way in which it is produced. For this same reason it is allowable to ascribe to the windings so small a resistance that they do not carry any appreciable charges.

Then no other but electromagnetic forces will act on the windings of the coil and these cannot give rise to any couple about the axis PQ , because such forces are perpendicular to the elements of the windings. By the theorem of § 13 the couple acting on the torsion-balance must therefore have been equal and opposite to the moment of rotation, acting on the condenser-plates and the wire W . It remains to show that this last moment has been 0.

I shall denote by I the electromotive forces acting in the connecting wire W , by II those existing in the windings of the coil, and I shall distinguish by the suffixes 1 and 2 the states arising from these two causes. Let us indicate by A_1 the charges of the plates and the currents in these and the wire W , in so far as they are due to I, and let A_2 have the same meaning with respect to II; also, let F_1 and F_2 be the electromagnetic fields excited by the two causes. In each of these fields there will be an electric force \mathfrak{d} (acting on charges that are in rest), as well as a magnetic force \mathfrak{h} ; in virtue of the first, the field will exert a ponderomotive force on the charges of the plates and in virtue of the second on the currents, one of these actions being determined by the first, and the other by the last term in the general equation (VII). If we denote by the symbol (F, A) the couple acting on the plates and the wire, in so far as it is due

to a field F and a state A of these bodies, the two actions we shall have to consider may be represented by

$$(F_1, A_2) \text{ and } (F_2, A_1).$$

The first of these is readily seen to be 0. Indeed, the magnetic field, produced by the forces I , though modified by the presence of the dielectric ring, is symmetrical around the axis PQ . Therefore, if the periphery of the condenser-plates is nowhere interrupted, the state A_2 will consist in circular currents in these plates, without any electric charge. It is impossible that the field F_1 should, by its action on these currents, give rise to a couple, since, whatever be the nature of this field, each element of the stream-tubes will only be acted on by a force perpendicular to its length.

In reality the case was somewhat different, each condenser-plate being cut by a vertical slit. There must have been equal and opposite charges at the edges of each slit and the field F_1 must have acted on these charges, in virtue of the electric force existing in it. These forces may however be supposed to have annulled each other, because the distance between the charges on the two edges was very small.

§ 16. The action (F_2, A_1) is therefore the only one that remains to be considered. Now, in the state A_1 , the plates of the condenser were the seat of charges, whose amount was modified by the influence of the dielectric ring, and whose alternations were accompanied by currents in the wire W and in part of the plates themselves. In so far as they are currents of conduction, i. e. in so far as they consist in a motion of electrons, these currents are evidently unclosed. We may decompose the whole system of them into infinitely thin stream-tubes, the tubes being all thronged together in the connecting wire, and widening out in the plates, at whose surfaces each stream-tube ends in two elements of surface.

Let S be one of the stream-tubes, G the end of it on the outer, and H that on the inner plate, e the charge in G , $-e$ that in H ,

$$i = \frac{de}{dt} \dots \dots \dots (23)$$

the current in the tube in the direction from H towards G , and let us consider the action (F_2, A_1) only in so far as it depends on this current i and on the charges e and $-e$.

In the first place there will be an electromagnetic force on the tube S , owing to the current i . The couple arising from it depends on the course of the magnetic lines of force in the field F_2 ; it is most easily found by remarking that its work during a complete

revolution of S about the axis PQ is numerically equal to the product of $\frac{i}{c}$ by the number of lines of force that are cut by S . These lines are precisely those that are intersected by the surface described by S in its revolution, a surface which may have different forms, according to the form of the wire W , but has at all events for its boundaries the circles described by the points G and H . Let N be the number of these lines, taken positive if the middle one of them passes *upwards* along PQ , and let us take as positive directions for the rotation and for the couple the direction corresponding to the upward direction. Then, for a full revolution in the positive direction, the work of the couple will be $-\frac{1}{c}iN$, whence we find for the couple itself

$$-\frac{1}{2\pi c}iN. \dots \dots \dots (24)$$

If this were all, we should indeed come to an effect such as was expected by WHITEHEAD. We must however keep in mind that there can never be a variable magnetic field without *electric* forces. Such forces, represented in direction and intensity by the vector \mathfrak{d} , will exist in the field H , the lines of electric force being circles around the axis PQ .

We must therefore add to (24) the couple arising from the action of the field on the charges e and $-e$; its moment may again be found by considering the work done in a complete revolution in the positive direction.

The force on the charge e being $e\mathfrak{d}$, its work is equal to the product of e by the line-integral of \mathfrak{d} along the circle described by G . Similarly, the work of the force acting on the charge $-e$ in H is the product of $-e$ by the line-integral of \mathfrak{d} along the circle described by H , or, what amounts to the same thing, the product of $+e$ by the line-integral for this circle, if it is taken in the negative direction. Now, if we follow the circle G in the positive and the circle H in the negative direction, we shall have gone along the whole contour of the surface described by the stream-tube S , in a direction corresponding to the positive direction of the magnetic force. Hence, by a well known theorem, of which the fundamental equation (VI) is the expression, the sum of the two line-integrals by which e must be multiplied, will be

$$-\frac{e}{c} \frac{dN}{dt},$$

and the couple to be added to (24) will be given by

$$-\frac{1}{2\pi c} e \frac{dN}{dt}.$$

Taking into account (23), we find for the total couple

$$-\frac{1}{2\pi c} \left(iN + e \frac{dN}{dt} \right) = -\frac{1}{2\pi c} \frac{d(eN)}{dt}.$$

Since this is the rate of change of a periodic quantity, the mean value will be 0, as above asserted.

The above somewhat complicated reasoning has been used in order to avoid the difficulties arising in a closer examination of the phenomena going on in the ponderable dielectrics. The result may however be verified by making suitable assumptions concerning these phenomena. It will suffice for our purpose to replace one of the dielectric bodies by a single pair of electrons *A* and *B*, the first of which is immovable, whereas the second may be displaced over an infinitely small distance, in a radial direction, by the electric forces of the field F_1 . We shall denote by $-e$ and $+e$ the charges of *A* and *B*, by r the distance of *A* to the axis, by s the infinitely small distance *AB*, and we shall write h_z for the vertical component of the magnetic force in the field F_2 and D for the value of the dielectric displacement in this field at a distance r from the axis. We shall take the positive directions as follows: for s outwards, for h_z upwards, and for D along the circular line of electric force in a direction corresponding to the positive direction of h_z , i. e. in the direction of a positive rotation about the axis.

Now, owing to the velocity $\frac{ds}{dt}$ of the electron *B*, there will be, according to the formula (VII), a force

$$-\frac{e}{c} h_z \frac{ds}{dt}$$

acting on this electron along a circle about the axis, and producing a moment

$$-\frac{e}{c} r h_z \frac{ds}{dt} (24')$$

This is the couple of which WHITEHEAD has sought to prove the existence. It is however annulled by the moment arising from the action of the field F_2 in virtue of its electric force D . For the particle *A* this moment is

$$-e r D$$

and for the particle *B* it is obtained if we replace $-e$ by $+e$,

taking at the same time the value of rD at the distance $r+s$ from the axis.

The algebraic sum of the two moments will therefore be

$$e s \frac{\partial}{\partial r} (rD)$$

and for this we may write

$$-\frac{e}{c} s r \frac{\partial h_z}{\partial t}, \dots \dots \dots (24'')$$

since, by the equation (VI)

$$\frac{\partial}{\partial r} (rD) = -\frac{1}{c} r \frac{\partial h_z}{\partial t}.$$

For the sum of (24') and (24'') we may write

$$-\frac{e}{c} r \frac{d(s h_z)}{dt},$$

whence it is immediately seen that its mean value is 0 for a full period.

Physics. — *Methods and apparatus used in the cryogenic laboratory.*

III. Baths of very uniform and constant temperature in the cryostat (continued). A cryostat of modified form for apparatus of small dimensions. IV. A permanent bath of liquid nitrogen at ordinary and at reduced pressure. V. Arrangement of a BURCKHARDT-WEISS vacuum-pump for use in the circulations for low temperatures. Communication N° 83 (continued) from the Laboratory at Leiden. By Prof. H. KAMERLINGH ONNES. (Read February 28, 1903).

III. § 6. *A cryostat of modified form for apparatus of small dimensions.* If the cross sections of the apparatus that is to be immersed into the bath are small, vacuum glasses may be profitably used in the construction of the cryostat. For, vacuum glasses of comparatively small diameter can then accommodate the stirrer and the temperature indicator in addition to the measuring apparatus. Plate IV shows a cryostat of the kind, viz. the one used in the determinations by HYNDMAN and myself on the critical state of oxygen.

Obviously the arrangement could be much simpler, as it was not necessary to watch the liquefied gas streaming from the jet or to use the generated cold vapour for the cooling and as no particles of dust from the leads had to be feared, a filter was not required. (Comp. Comm. 51, Sept. '99 § 2. Y_1 p. 12). The principles for obtaining a uniform con-

stant temperature, laid down in the previous communication have all been applied in this arrangement, a vigorous stirring with the ring shaped valved-stirrer, the adjustment at the desired temperature to the indication of a sensitive indicator by regulating the pressure at which the liquid boils while reading a differential oil-manometer made for the purpose, and lastly the determination of the temperature of observation as corresponding with the mean obtained graphically of the readings of the thermometer (as in § 5).

Plate V shows in detail the differences in the construction between this form and the former plates I and II (and also Plate I Comm. 51), the parts unaltered remaining are indicated by the same letters as before, and the modified parts by letters with accents, while entirely different parts have new letters.

The height of the vacuumglass B'_0 , is so chosen that the liquefied gas cannot be blown out; and the glass itself has been silvered, leaving open two opposing windows V'_2 . Through these the phenomena in the experimental tube may be watched, and from the position of an aluminium wire fastened to a cork float the depth of liquefied gas may be derived. If the insulating power of the vacuumglass is not perfect, condensation of moisture on its outer wall may be avoided by placing it into a beaker filled with alcohol, which if necessary is renewed when cooled. Thus the same principle is followed which was employed when necessary in the case of the cryostat (Comm. 51) when the windows had to be kept clear and where hot dry air was drawn through the outer spaces of the observing glasses (V_2 , see Pl. I of this Comm. and for the details pl. I Comm. 51).

The vacuum glass and the auxiliary apparatus are supported by a copper cover N'_{00} , with its rim tinned to protect it from the action of the india-rubber ring N'_1 , and which, like the cryostat of § 1, has been coated with polished nickel-paper. To this cover are fastened the exit tube of the gas T'_{12} and the safety tube Y'_{22} , the connection X'_2 with the oil manometer (for details see plate I) and a copper tube N'_{01} , into which the india rubber stopper is placed holding the apparatus to be immersed in the bath (in our case the piezometer for the critical phenomena K_7 , and the correction thermometer ζ_{01} with its leads ζ_{00} (comp. § 1) while the thermo-element Θ may be considered as forming an inherent part of the cryostat). There is also a tube through which the capillary a_1 admitting the liquefied gas is led and where it is supported by a piece of cork a'_{13} . It is closed by means of an india-rubber tube a'_{12} drawn over the tube and a thin cap soldered on to a_1 .

Between the cover and the rim of the vacuum glass a wooden

cylindrical jacket N'_3 is placed resting against the latter by means of an india-rubber ring N'_2 . Two cylinders N'_4, N'_5 of nickel-paper serve to diminish radiation, especially in the direction of the delivery tube.

As mentioned the frame which keeps the protecting cylinder in its place is fastened to the cover. For a complete explanation of the letters and parts of both this and the stirrer reference may be made to § 4. Further we may note that ξ_1 is fastened with silk cords to ξ'_2 and this again with silk cords to the cover N'_{00} , while ξ'_2 is supported by the glass tube ξ_3 fitting onto the pins ξ'_5 .

The three threads χ_1 on which the stirrer hangs are led directly through the three india-rubber tubes χ'_{61} , connected hermetically to tubes soldered onto the cover and fitting hermetically onto the threads at χ'_{62} , to the brass disc χ'_{63} and rod χ'_{64} which is connected by a small chain χ'_{65} passing over a pulley χ'_{66} to the motor by means of a steelwire. The arm of the motor may be adjusted to different throws, while velocity of rotation can be regulated by means of a rheostat.

The mounting of the apparatus is very simple. The stopper with the measuring apparatus is placed into the tube N'_{01} of the cover, to which all the auxiliary apparatus has been connected, then the vacuum glass is slid into the india-rubber ring which is also connected to the cover and is fastened there by means of tightening bands. In order to secure an airtight fit the india-rubber on the metal and on the glass has been coated beforehand with a solution of indiarubber in benzine.

With a view to the description given in III the operations for the adjustments at given temperature require amplification only in a few points. In the case considered here, the evaporated gas was led back through the exit tube to the gasholder or to the large exhausted reservoir of the ethylene circulation in the cryogenic laboratory (Comm. 14, Dec. '94) whence the ethylene was further condensed into the condenser immersed in methyl chloride. As described in Comm. 14 the circulations of the cryogenic laboratory have been so arranged that they may be used at any time. Besides the reservoirs that have to be exhausted, a permanent part of the circulation consists in branched tubes with cocks as shown on plates I and IV. The cryostat had only to be connected to the circulation in order to be easily brought to the required pressure. In the case considered here the experiments were not made in the cryogenic laboratory but in an other room and the length of the lead a'_{31} was 10 m. Although the liquid ethylene had to be conducted over such a distance, yet

the adjustment of the bath to the required temperature (say at -120°) was obtained within one hour after the pumps in the cryogenic laboratory had been set working.

Instead of a resistance thermometer, to regulate the temperature, we used the thermoelement Θ , the protected junction being placed at the side of the piezometer (comp. comm. 27 June '96); it is visible through the window V'_2 (in plate IV). The electro-motive power of the thermoelement is compared by means of the zero method with that of a thermoelectric control element or a WESTON-element.

For the same difference of temperature the deflections on the scale of the sensitive galvanometer were almost as large as in the measurements made with the resistance thermometer (comp. § 5). An example of the determination of the temperature is not necessary in addition to Plate III.

IV. *A permanent bath of liquid nitrogen at ordinary or reduced pressure.* In Comm. 14 (Dec. '94) a short description was given of the temperature steps obtained by means of circulations of methylchloride, ethylene and oxygen. In connection with that description I mentioned my intention of adding more circulations to those already existing and said that I hoped to replace more and more parts of the existing circulations by greater and to insert such technical apparatus as should be found advisable so that the existing apparatus could be used in the new circulations with pure or costly gases. An example of this is the circulation of nitrogen added to the existing temperature cascade, of which a description is now required by the completion of some of the measurements rendered possible by it. For measurements at temperature between -195° C. and -210° C. a nitrogen is much to be preferred to an oxygen-circulation as the tension at which the oxygen boils at -195° is so small that accurate regulation at constant temperature becomes very difficult. As the preparation of pure nitrogen in such large quantities as a circulation requires presents many difficulties, the compressor and the vacuum pump must be suitable and efficient. These conditions are fulfilled by the mercury and the auxiliary compressors which are generally used for the compression of pure gas and which in the originally temperature cascade served for the oxygen circulation. However when the BROTHERHOOD-compressor (comp. Comm. 14 Dec. '94 and 51 Sept. '99) could be used for the oxygen circulation in the cascade they could be used for the nitrogen circulation.

The nitrogen is prepared from sodium nitrite. Besides being passed through ferrous sulphate and sulphuric acid it is led over hot cop-

per and then again through ferrous sulphate and sodium hydroxide, because otherwise traces of nitric oxide might be left and this blocks the cocks (this gas is recognised at once by a strong smell of higher oxides of nitrogen when it mixes with the air). In order to remove traces of this oxide, I have sometimes added to the gas a quantity of oxygen as nearly as possible equivalent to the NO contained therein and have then passed it through sodium hydroxide. The gas is collected and provisionally kept in galvanised iron vessels holding 1 M³. From these it is driven out later by water heated by a steam jet and after passing through sodium hydroxide and sulphuric acid it is forced into a small gasholder floating on oil and holding 500 L. By means of the auxiliary compressor *AC* lubricated with glycerine (see Pl. VI and for details Comm. 54 Sept. '99) and the mercury compressor *HgC* (see Pl. VI and for details Comm. 54) the gas is forced over into a metal cylinder of 18 liters capacity after passing through the drying tubes *D*₁, *D*₂ filled with caustic soda in the form of sticks.

Plate VI shows the scheme of the entire circulation with the cryostat *Cr*, into which the liquid nitrogen is admitted at *a* and where it evaporates under ordinary or reduced pressure at the desired temperature. The whole arrangement has been used in the comparison of the platinum resistance thermometer with the hydrogen thermometer, which has been mentioned in III. The apparatus themselves are drawn diagrammatically but in their true proportions, while the connections are entirely schematic. A detailed representation of the cryostat with the auxiliary apparatus appertaining to it for uniform and constant temperatures will be found on plate I where the same letters have been used. On the other hand plate VI may be considered as a supplement to plate I. Nothing is wanting for a complete representation of the circulation except the gasholder and the vacuum vessel of 5 M³. (comp. § 5 for its use) which are too large to be represented on the same drawing as the parts given. There is an insignificant difference in the coupling of the leads between plate I and plate VI, for on plate VI *Exh.* 1' indicates the connection of the compression side of a BURCKHARDT—WEISS vacuum pump *Bu Vac.*, described below into which the exhaust *Exh.* 2 terminates, to an exhaust pump (which may also be *AC* of the circulation). Moreover next to the lead from *Y*₁ to *Y*₃, we have drawn what must be substituted for it in comparison with the arrangement on plate IV.

RN is the cylinder where the nitrogen has been compressed by means of *AC* and *HgC* through the drying tubes *D*₁ and *D*₂, while *Gas* indicates the 500 liter gas holder floating on oil. The nitrogen may

be admitted at the required pressure into the condensation spiral CS from the cylinder RN through a final drying tube D_3 containing phosphoric anhydride, as well as directly from the compressor. The spiral is placed in a vacuumglass B with a protecting cylinder A . Liquid oxygen is admitted into B through $Ox.liq$ from the oxygen circulation of the cryogenic laboratory, viz. from the condensation spiral which is cooled in the ethylene boiling flask (Comm. 14, Dec. '94). The oxygen escapes through $Ox.vap$, a wide safety tube S being connected in the ordinary way, and is compressed into the spiral by a BROTHERHOOD-compressor which is lubricated with glycerine and arranged as described in Comm. 51. It may be remarked that, with a view to the possibility of an explosion of a glycerine mist mixed with oxygen, the pressure in this operation is not raised above 80 atmospheres. (Comp. the explosion described in the Zeitsch. f. Kohlensäure Industrie 1903).

The nitrogen condenser itself has been drawn in detail on plate VII. In so far as the parts correspond — either with plate V for the cover, or with plate I of Comm. 51 for the regulation cock described there — the same letters have been used, but as some of the parts differ a little the letters have an additional accent. As in the case of the small cryostat plate V, the cover is coated internally with nickel-paper, while the upper turns of CS are protected again by a ring of paste board and nickel-paper. The condensation spiral consists in the condenser proper CS_2 and the regenerator CS_1 ; here the same principle has been applied which has been followed in the cryogenic laboratory from the first (Comp. Comm. 14 Dec. '94); the vapour of the oxygen is forced by the cylinder B''_2 which is closed at the bottom with the stopper B''_{30} to pass along the regenerator spiral. As in the ethylene boilingflask (see comm. 14 Dec. '94) the level of the liquid oxygen in the glass tube W is indicated by a cork float dr_1 with a steel capillary dr_2 to which a thin reed d_3 is fastened; the steel capillary passes through a glass tube B'_{31} .

Liquid nitrogen flows out through the fine regulatingcock $h h_3$ of the same kind as that through which the liquid gas is admitted into the cryostat. For the description of this cock compare Comm. 51 and 54.

It may be added that Gaz' shows the connection with the auxiliary apparatus described in Comm. 54 for operations where HgC is used, which connection make it possible for the gas to stream back to the gasholder Gaz .

V. *Arrangement of a BURCKHARDT-WEISS vacuum pump to be used with a circulation for low temperature.* The well-known excellent

vacuum pump patented by BURCKHARDT and WEISS has been first used, I think by OLSZEWSKI, for removing the large volumes of gas which rise from a bath of liquefied gas at a reduced pressure. We shall now speak of some modifications and auxiliary apparatus by means of which the perfect purity of a gas is secured in a high vacuum. A pump arranged in this way may also be introduced into circulations of costly gases. In our laboratory it has been worked very satisfactorily for many years. A diagrammatic figure of the entire BURCKHARDT-pump has been given on plate VI *Bu. Vac.*, the pump cylinder with its slide valve box, the beginning of the suction- and the delivery tubes with the auxiliary apparatus belonging to them are shown on plate VIII, where fig. 1 gives the side elevation, fig. 2 the top elevation and fig. 3 the section. The well-known working of the piston and the valve, the successive communication of the valve ports 5 and 5', each individually by means of the slide hole 2 with the suction valve port 1 or with the delivery valve port 4 and together by means of the ring-shaped opening 3 may be seen without further comment from the section. The pump displaces 360 M³ an hour, hence, when exhausting at a pressure of 2 c.m., about 10 M³ gas, measured normally can circulate. At Leiden it is used almost exclusively with an additional vacuum pump exhausting at the compression side. It exhausts then till 2 m.M.

As a lubricant and for the airtight fittings to be described in the following pages, only bone-oil is used which after having been tested at the exhaust pump has proved to have no perceptible vapour pressure.

For the technical work ordinary ring packings are quite sufficient, I have, however, replaced them by folded packings as described in Comm. 54 Jan. '00 for the compressor and the auxiliary compressor. The leather ring of the packing is supported there as in Plate IV b_{14} by the india rubber ring b_{42} (for an exhausting packing comp. E_{12} Pl. VII fig. 3 Comm. 54). The packing cylinders have been made long enough to contain two folded packings (one for exhausting and one for compression) and a bronze tightening piece, but as a rule they only hold the packing for exhaust.

New additions are the vessels O_1 and O_2 see also plate II filled with oil (or with glycerine for those gases which cannot be used with oil); they serve to protect the packing cases of the cylinder and the slide valve box entirely from the atmosphere and also to cool the piston rod. The covers O_{10} and O_{20} protect the lubricant against dust or moisture.

For the oil holders S_1, S_2 we have chosen the construction explained in detail in fig 7. S_{12} is an ordinary oilpot for visible cylinder lubri-

KAME

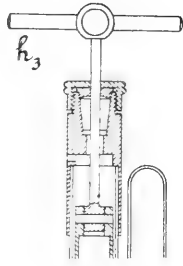
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Fig. III.



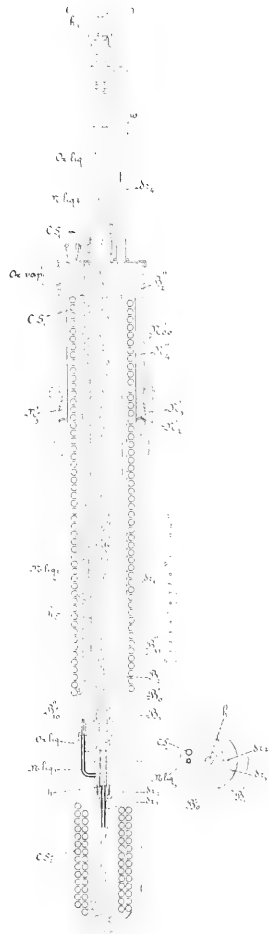
H. KAMER

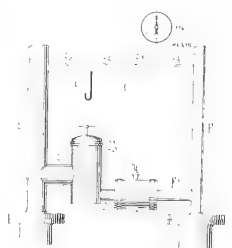


D

H. KAMERLINGH ONNES. Methods and apparatus used in the Cryogenic Laboratory. IV. Permanent bath of liquid nitrogen

Pl. 17





cation in vacuo. The cover S_{128} has been tightly screwed on the hollow rod S_{1290} and presses the glass S_{1221} hermetically on to the packings. By means of the winged nut S_{123} the point is adjusted so that the oil drops regularly through the openings S_{1291} into the space S_{124} which communicates with S_{126} through S_{125} and which may be watched through the glass windows in S_{124} . For our purpose the oil holder S_{12} is placed on a stout tube S_{13} onto which by means of india rubber rings and tightening bands the glass cylinder S_{11} is fixed on a copper bottom, soldered to S_{13} . The glass cylinder is filled with oil and covered with a lid S_{15} . By means of S_{122} new oil can be admitted from the reserve vessel into the lubrication vessel. In this way the air is sufficiently prevented from entering the lubrication apparatus.

Lastly, between the exhaust tube z and the compression tube p a safety valve has been placed, which prevents the pressure on the compression side from rising above a certain height (usually $\frac{1}{4}$ atmosphere). Hence it is possible to let the pump work on and to open and shut the cocks as the work requires. The noise of the safety valve gives warning that the cocks have not been properly used. In any case no difficulty is to be feared if the possible output of the pump might diminish in any way in relation to the intake. Fig. 4 shows a diagram of this connection, some of the parts being drawn to proportion; fig. 6 shows a section of the safety valve case itself.

The side tube p_1 is connected by a joint K with the tube v_1 which opens into the space below the safety valve. The space above the safety valve communicates with the exhaust tube through the side tube z_1 . The broad valve v_3 is coated at the bottom with an india rubber sheet which presses against the narrow rim v_4 . The spring v_5 is stretched with the key v_7 while the plate v_8 with the nut v_{61} and packing is tightly screwed on to the rim v_{10} . The packing cylinder v_{11} , like the packing just mentioned is kept under oil; a cover v_{12} above it protects it from dust.

The connection K between the tubes p_1 and v_1 could not be brought about with flanges or with screw joints without causing tension in the tubes. Therefore it was made in the following manner as shown by fig. 5. A widened piece k_1 is soldered on p_1 , v_1 fitting into this piece. The india rubber connection k_2 is kept in oil; for this purpose a rim k_3 was used which was soldered on to p_1 and a rim k_4 which was soldered on to z_1 . Over these rims a wide piece of tubing k_5 is drawn which is fastened to k_3 and k_4 by means of india rubber rings k_6 k_7 and tightening bands, and forms together with these an oilreservoir.

Besides being connected through the safety valve case and the above mentioned connection, the compression tube and the exhaust tube are also connected (comp. again the diagrammatic fig. 4, as an explanation of figs. 1, 2, 3) by the cocks r_1, r_2, r_3, r_4 and may be connected with an airpump l , an indicator i and a vacuummanometer m . The use made of this auxiliary apparatus in regular working or in preparing, mounting, testing, drying and exhausting the pump, requires no further explanation. As a matter of course, the pump is not introduced into a circulation unless it has worked for a long time with the exhaust- and compression sides closed and no change has been found in the vacuum.

I further remark that the principle of an oilconnection as illustrated by fig. 5 may be profitably applied when wide tubes have to be connected, which have neither flanges nor nuts and joints or in cases where it is not advisable to make these contrivances. The method then to be followed is illustrated by fig. 8 where K'_1, K'_3 and K'_4 are loose pieces slid on the tubes b_1 and b_2 , which we want to connect. A good fit is obtained by means of the india rubber rings $K'_{21}, K'_{22}, K'_{31}, K'_{32}, K'_{41}, K'_{42}$, under brass tightening bands. K'_{91} and K'_{92} serve to admit and to run out the oil. In this way one always succeeds in making within a short time an airtight fit. For the connection of the pump tubes to the conduit at f'_1 and f'_2 (comp fig, 1) this method has been used in a manner which will be clear from the figure.

Physics. — Communication n°. 84 from the Physical Laboratory at Leiden "*Isotherms of diatomic gases and their binary mixtures. V. An accurate volumenometer and mixing apparatus.*" (By H. KAMERLINGH ONNES and H. H. F. HYNDMAN).

§ 19. *A compression tube of larger dimensions.* In § 6 of Comm. n°. 69 March '01 we have explained that the apparatus described in §§ 3 and 4 hardly gave the accuracy required in the determinations of density, if the total quantity of compressed gas was smaller than 5 cc. Since, however, at most 600 cc. of gas under normal conditions is available in this apparatus it is not suitable for densities of more than 120 times the normal.

On Pl. I a compression tube is shown which has about three liters capacity and hence which is suitable for measurements up to densities of some 500 times the normal and with at least the same accuracy as the above. The drawing is, as usual, schematic in

the connections but the individual parts are drawn to scale, it can be compared with Pl. I of Comm. n^o. 69. For those parts which correspond the same letters are retained, where an alteration has been made the letters are accented, while new parts are characterised by new letters. A detailed description is hence unnecessary, but it may be noted that the screw head a_4 is changed, that a closed nut screwed on at c_{121} has been added by which the pressure can be suddenly released if necessary, and that a cock c_{15} has been introduced, to enable the level glass to be shut off if required.

The compression tube A'_1 is designed for use in the first place with piezometers of the kind described in § 2 but of larger dimensions. The use of this tube A'_1 is then the same as the original A_1 (comp. §§ 3 and 4) and it may be introduced directly in place of this into the system shown on Pl. I of Comm. n^o. 69.

In the second place this compression tube serves to hold glass tubes with a stem b_4 — b_5 (cf. Pl. II fig. 2 Comm. n^o. 69) onto which other apparatus can be screwed in place of the simple nut and capillary shown there. In Pl. I fig. 2 is shown a three way cock with two steel capillaries g_1' and g_1'' which is employed as follows.

One of the capillaries g_1' is connected directly with the small measuring piezometer of the type of f fig. 2 Pl. II Comm. N^o. 69 the other g_1'' with a volumenometer, so that when k_{110} is shut and k_{130} and k_{120} are open a known quantity of gas can be brought into the compression cylinder from the volumenometer. On the other hand when k_{110} is open and k_{130} shut this gas can be compressed into the piezometer where the temperature and pressure are measured as before. The large glass tube with stem and the piezometerreservoir, form in this way a piezometer of variable volume (constant quantity) and the difference with the former method consists in the measurement of the normal volume in a volumenometer instead of in the piezometer itself. The volume of the large glass tube in this method is not required to any high accuracy and the small u tube at the bottom may be omitted (g_1 Comm. n^o. 50 Pl. I fig. 4 June '99 and b_2 Comm. n^o. 69 Pl. II March '01). The accuracy is now really that obtainable with the volumenometer (cf. § 20) in so far as the determination of the normal volume is concerned. The spaces k_{001} , k_{130} , k_{120} of the small three way steel cock must be also accurately calibrated. Care is taken also that the pins really shut properly into the sockets which makes the whole absolutely trustworthy up to at 100 At.

Although we wish to confine ourselves to the method of variable volume (constant mass) a second measurement with the volumenometer

meter is required, in the same manner as would be necessary if we employed the method of constant volume. For, we have already mentioned in § 1 that this compression apparatus is suitable for this method. The measurement is made by shutting k_{110} under known pressure and allowing the compressed gas to expand through the capillaries g_1'' and g_1' into the volumenometer and reading as before. This second volumetric measurement, with its necessary corrections, gives the determination of the normal volume after the measurements at high pressure and compares with the second normal volume determination of the original method.

§ 20. *An accurate volumenometer.* The volumenometer mentioned above in § 19 was designed to give isothermal measurements of an accuracy of $\frac{1}{10000}$ up to 60 Ats pressure. Hence the same accuracy was desired as with the standard piezometers of Comm. n° 50 June '99, while at the same time the determination of the deviations from BOYLE'S law at ordinary pressures was kept in view. The most analogous apparatus is that employed by LEDUC; that of WITKOWSKI, who has used a form more closely analogous with ours, does not appear to have been designed for high accuracy.

The measuring vessel E_b (Pl. II fig. 1 and more in detail fig. 2) where the gas is shut off by mercury entering through $E_{b_{01}}$ consists principally of 5 bulbs E_{b_1} such of 250 cc. and a smaller bulb E_{b_2} of 25 cc. capacity. These are separated by short really cylindrical portions $E_{b_2} \dots E_{b_5}$, on each of which there is a mark, near to which the mercury meniscus is brought for the measurements.

At the lower end of the measuring vessel is a contrivance after the scheme of Comm. n°. 27, for catching any dust or stray gas which may perchance come from the rubber tube at Cl_1 Pl. II fig. 2. At the upper end the vessel terminates in a capillary tube $E_{b_{90}}$ which is divided almost immediately into two $E_{b_{91}}$ and $E_{b_{92}}$. One of them is terminated near the apparatus by a cock r_5 . The other ends in a glass or steel capillary terminated also by a cock. On Pl. II fig. 2 e. g. the volumenometer is connected to the mixing apparatus F by a capillary tube soldered on to it after it has been mounted in E_a by the cock r_6 . At $E_{b_{93}}$ (Pl. II fig. 1) e. g. r_9 the steel capillary g_1'' proceeding from the three way cock mentioned in § 19 may be connected. The small bulb E_{b_2} is calibrated by mercury at the same time as the larger and serves to determine the small volumes above $E_{b_{92}}$.

To keep the temperature of the gas constant and uniform the measuring vessel is firmly fixed to the bottom of the copper case E_{a_0} .

through which water at constant temperature flows from the thermostat described in Comm. n°. 70 III May '01 (see E_{a_2} on Pl. II. fig. 1). Uniformity of temperature is also assisted by the movement of the stirrer on to which the thermometer Th is fixed.

The ring E_{a_0} together with the bottom plate is soldered to the case E_{a_0} and is large enough for the measuring vessel to be put through it. The closing plate E_c is made fast to the measuring vessel and is so arranged, that it can easily be made watertight and that it can bear the weight of the whole mass of mercury when the tube is full without any danger to the glass as long at least as it is not displaced from its vertical position. The closing plate with flange and packing is pressed against the ring E_{a_3} at the bottom of E_a by the screw E_{c_1} . The different parts will be seen by an inspection of Pl. II fig. 1. E_{c_2} the ring and packing, made large enough to be brought over the measuring vessel, E_{c_4} and E_{c_5} round copper plates provided with a thread and cut out at E_{c_4} and E_{c_5} enough to pass over the tube E_{b_0} , so that they can be put on from the side and made fast together by the screws E_{c_3} ; together they form the closing plate which is screwed into E_{c_2} ; E_{f_1} and E_{f_2} the halves from a round vulcanite plate which rest on the ring E_{c_3} with bottom E_{c_4} and support the enlargement $E_{b_{01}}$. E_{f_2} and E_{f_3} the two halves of a rubber plate which are united by rubber solution and pressed into the ring E_{c_2} to make the whole watertight.

When the closing plate has been made fast perpendicularly to the measuring glass and has been screwed against the lower rim of E_a , the two parts of the conical top E_m are brought together into place and the measuring glass centered and held fast by the cork E_k . The whole waterbath is then brought into as vertical a position as possible.

There are windows in the case E_a which enable the tube to be lighted and read. These are formed by thin pieces of plate glass held between stout brass frames E_{h_1} and E_{h_2} one of which is soldered to the wall of E_a . The screws E_{h_3} enable the plate to be equally pressed against the rubber packing E_{h_5} and the glass. It is quite necessary to have the case completely tight, which was here obtained, to prevent the felt in which E_a is packed from becoming wet, and hence from an irregular loss of temperature.

In spite of the verticality of the entire case the glasses require to be tested with a contact spirit level, in order that the necessary correction to the cathetometer reading may be made.

To determine the volume of an enclosed quantity of gas the position of the meniscus is not read with reference to the marks on the glass

tubes, but on finer lines etched on to small glass plates E_{91} — E_{97} , provided with connections E_{90} and screws E_{91} to fix them to the cylindrical portions of the measuring vessel. By a proper arrangement of these the meniscus and the lines can be sharply seen over the whole length of the case.

The measuring vessel is calibrated by temporarily blowing on, at the lower end, a small glass cock with a fine point (cf. Comm. N^o. 70. IV. May '01). The mercury is introduced through this in the carefully exhausted apparatus and the menisci are then read in the manner described above for the measurements and with the same precautions as to lighting and temperature. The mercury drawn off at the cock is weighed. As before the readings are made on the glass plates but in order that the calibration shall not be lost if these have to be removed, they are also compared with the lines on the cylindrical tubes. This would be necessary if the tube had to be removed cleaned and dried after the method of Comm. N^o. 27, but usually it is sufficient to suck up the various liquids and to dry by repeated evacuation admission of dry air through r_6 and r_1 of Pl. II fig. 2.

The measuring vessel can be completely shut off from the mercury reservoir, see Pl. II fig. 2 or the manometer by the clamp Cl_1 . All these connections are carefully cleaned good thickwalled black rubber tubes, which are strengthened by wrapping them spirally in strong tape. The mercury meniscus (cf Comm. N^o. 67 Dec. '00 for what is here implied) remains quite clean after a series of measurements, if only dry gas is admitted to the volumenometer (this is only true when the gas has no action on the fat of the cocks and joints). The small changes in the position of the meniscus to bring it to the required position are made by manipulating the clamp Cl_3 and the reservoir. During the measurements this clamp is always closed.

The pressure of the gas in the volumenometer is given by the height of the mercury in the manometer tube when Cl_1 is quite open. This is itself connected to a barometer and a reservoir at constant temperature by airtight connections in the manner of Comm. N^o. 60 June '00 and the same precautions are taken to ensure accuracy in the temperature determinations of these two mercury columns. The volumenometer meniscus and etched lines, manometer, barometer and standardscale (cf Comm. N^o. 60) are so placed that they can be read without altering the telescopes of the cathetometer.

The menisci of the barometer and manometer are read as described before, that of the volumenometer by the help of a brass plate with a 2 mm. slit in it, which is brought with a glow lamp to the same level as a meniscus and gives good definition.

In order that the required accuracy may be obtained it is necessary that the pressure shall not fall below 0,5 Atm.

To determine the theoretical normal volume measurements are made at two or if possible at three positions with the same quantity of gas. Whenever the third virial coefficient C (cf Comm. N^o. 71 June '01 and N^o. 74)¹⁾ does not come into account at the pressures considered and to the accuracy required, the same value of the coefficient B must be found by a combination of any two of the three measurements. This gives directly the deviations from the law of BOYLE and hence the theoretical normal volume.

§ 21. *The mixing apparatus.* On Pl. II fig. 2 the volumenometer described in § 20 is shown connected with other apparatus for the preparation of accurate mixtures of gases and for the investigation of their compressibility.

The drawings do not require much explanation. The mixing vessel F and the reservoir G have about 2 liters capacity. G is provided with a three way cock and is particularly useful when a number of mixtures are required with a small proportion of one component which can be contained therein.

The connecting tubes between r_5 , r_8 , r_9 and from E to r_6 are narrow so that the uncertainty of their temperature may have no influence on the accuracy of the measurements, the other tubes are large enough to allow free connection between the various parts and the pump and to help rapid exhaustion.

When a mixture of given composition is required, and the mercury stands above the closed clamps Cl_1 , Cl_2 , Cl_3 , Cl_4 , the whole apparatus is pumped out through r_1 and is filled through r_4 , while r_8 is shut, from say the gas apparatus connected to r_2 , after being washed out with this gas.

Then r_2 is shut and r_7 so turned that the gas is shut up in G while F is brought into connection with the pump through r_4 . The cocks r_8 , r_5 and r_6 are then opened and E and F and the connections pumped out again. By raising Kr and opening Cl_2 widely and Cl_1 (to prevent air entering from M) only partially the mercury is caused to enter E and to fill first $E_{b_{0.3}}$ without enclosing any gas, then E_b up to the required position, when Cl_1 is shut. The space between r_5 , r_2 , r_3 , r_1 is repeatedly washed out by a small quantity of gas from G through the cock r_4 , from here also gas is

¹⁾ Livre jubilaire dédié à J. BOSSCHA; Archives Néerlandaises, Ser. II. T. VI. p. 874—888. 1901.

brought into E and the whole pumped to a good vacuum. The required quantity of gas can then be brought into E through r_4 and r_5 . The volume temperature and pressure of the gas in E_a shut off by r_5 and r_6 are then accurately measured and when r_6 is opened nearly the whole of this can be brought over into F . The remaining portion in $E_{b_{90}}$ and $E_{b_{92}}$ is then measured by expanding to $E_{b_{82}}$ or $E_{b_{81}}$ and C_1 is again closed so that E can be again evacuated. The second gas is then brought directly into the volumenometer from r_3 and the volume measured in the same manner.

When this is finished r_6 is again opened and the second component in E mixed with the first in F where it stands for some time. The admixture of the total quantity is completed by drawing the combined gases several times backwards and forwards between the two vessels. The mixture is then preserved in F and as much as may be necessary is driven into E_b or through r_7 into other apparatus for measurements on the compressibility.

(April 24, 1903).

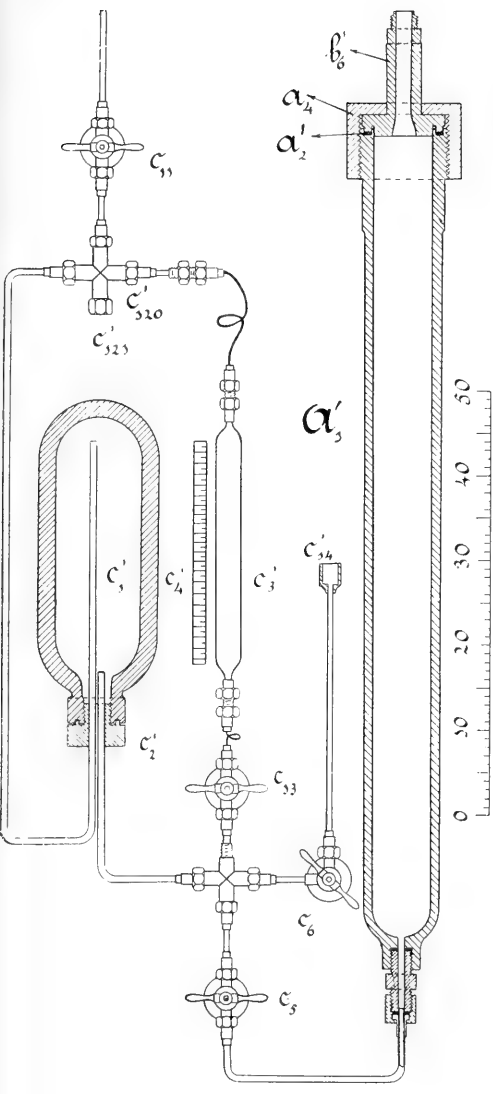


Fig. 1.

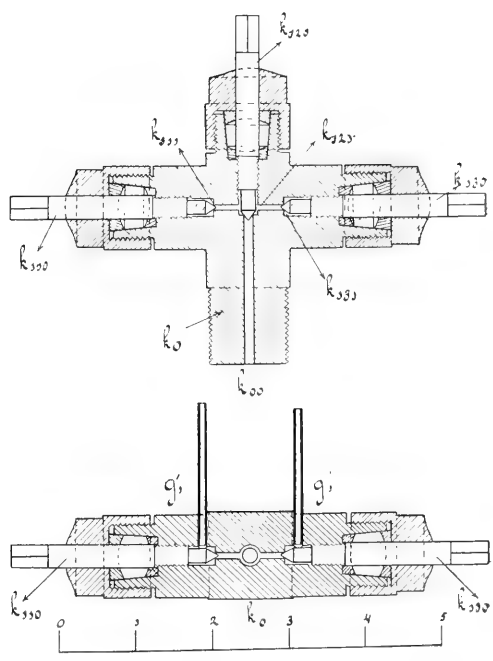


Fig. 2.

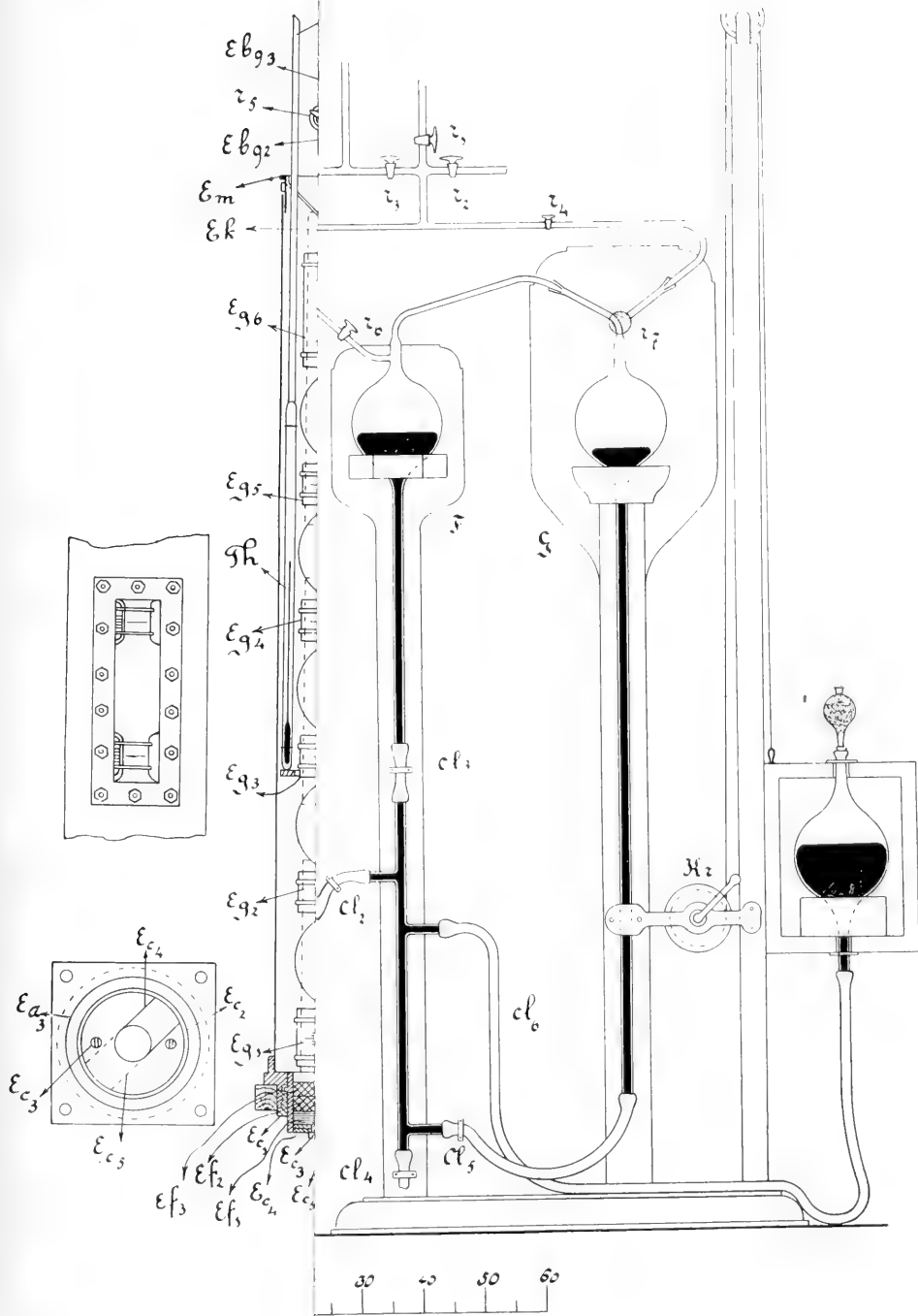


Fig. 2.



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Friday April 24, 1903.

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G. VAN ITERSON JR.: "The decomposition of cellulose by aerobic micro-organisms". (Communicated by Prof. M. W. BELJERINCK), p. 685, (with one plate).

The following papers were read:

Chemistry. — "*Dissociation in and crystallisation from a solid solution*". By Prof. C. A. LOBRY DE BRUYN and Mr. C. L. JUNGUS.

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

It is no longer necessary to be reminded of the analogy between liquid and solid solutions but it is still a matter of importance to trace and investigate new instances of the similarity of the two solutions. For this reason attention may be called to the following phenomena and observations.

The new phenomena relate to the interesting intramolecular rearrangement discovered by CIAMICIAN and SILBER¹⁾ in which solid or

¹⁾ Ber. 34. 2040 (1901).

dissolved *o*-nitrobenzaldehyde is converted, under the influence of the blue rays of sunlight ¹⁾ into *o*-nitrosobenzoic acid:



and where consequently an oxygen atom of the nitrogroup migrates to the neighbouring aldehyde group and oxidises the same to carboxyl. CLAMICIAN and SILBER have investigated this reaction more closely, principally with solutions in different liquids; as regards the transformation taking place in the solid condition, in which we happen to be particularly interested, they merely say: „dass die Krystalle nach und nach ihre lichtgelbe Farbe verlieren, undurchsichtig, grünlich und schliesslich weiss werden“.

The said changes in colour, the occurrence of the green coloration and the subsequent turning white render the phenomenon precisely significant for the knowledge of the properties of solid solutions. This will become evident when we think of the general and very interesting property of the organic nitrosoderivatives to suffer polymerisation and become colourless when in a solid condition; in solution, however, they are unimolecular and coloured (generally blue or green). This behaviour is quite comparable to that of nitric peroxide. In a certain number of cases the depolymerisation has been traced by cryoscopic means, as it often takes place very slowly: the lowering of the freezing point then gradually becomes greater while the colour becomes more and more intense. In this way it has been ascertained that in the colourless solid nitroso-compound two molecules have become united showing that an intense colour must be attributed to the single molecules. The same happens with NO_2 (the nitroso-compound of oxygen) which has an intense colour, whilst its polymerisation product N_2O_4 is colourless.

After these remarks it is not difficult to see in what manner the transformation of solid *o*-nitrobenzaldehyde into solid *o*-nitrosobenzoic acid must be conceived. The displacement commences as soon as the crystal is exposed to sunlight; after about 15 minutes a faint green tinge is perceptible which gradually deepens; the nitrosobenzoic acid, which is formed from and in the solvent, first remains in solid solution and, to judge from the green colour, in the unimolecular condition. On continuing the exposure to sunlight the colour becomes more intense, until finally the saturation point is reached; the outer

¹⁾ We have ascertained that an elevation of temperature does not cause the displacement.

layers of the crystal then become dull and a lighter green, the nitrosobenzoic acid, which crystallises out, is now however white and consequently bimoleculair¹⁾; finally the surface of the crystal becomes quite white and opaque. The process then apparently comes to a standstill because the sunlight cannot any longer penetrate the interior of the crystal or only in an insufficient degree. In this case the interior of a sufficiently big crystal still contains a green transparent nucleus.

The titration of five different specimens has given the following result:

After 2 $\frac{1}{2}$ day	about 3 ‰	of nitrosobenzoic acid.
" 6 $\frac{1}{2}$ "	" 5 "	" "
" 10 "	" 11 "	" "
" 15 "	" 15 "	" "
" 34 "	" 24 "	" "

The surfaces of the last crystals had turned quite white.

Conclusions as to the velocity of transformation cannot of course be drawn from these figures, as on the one hand the source of light varied too much in intensity, whilst on the other hand the crystals were of a different thickness.

It was considered of importance to try and determine the maximum solubility of *o*-nitrosobenzoic acid in *o*-nitrobenzaldehyde. From the surface of those green crystals, which commenced to deposit the white acid, the latter was therefore as far as possible removed by mechanical means. By titration 2.6 ‰ of nitrosobenzoic acid was then found; if now we may assume that the concentration of the acid inside the crystal is not smaller than that at the surface the saturated solid solution contains about 2.6 mols. of acid per 100 mols.

Another conclusion may still be drawn from the above, namely that *o*-nitrosobenzaldehyde is capable of forming mixed crystals with 2.6 mols. of *o*-nitrosobenzoic acid; whether these two substances are isomorphous is not known as the system of crystallisation of nitrosobenzoic acid has not been determined. Very probably they are not isomorphous as otherwise the power to form mixed crystals would occur over a larger interval or even for all proportions.

¹⁾ It has not been possible to ascertain, by the ordinary means at disposal, not even by the highest possible enlargement, that the *o*-nitrosobenzoic acid formed is crystalline. This cannot be a matter of surprise if we consider that the separation of the acid proceeds very rapidly and that the diffusion in solid solution is particularly slow. Still we may speak here of crystallisation as the separated substance, in contrast to amorphous compounds, exhibits definite physical constants (fixed melting point, solubility etc.).

By determining the meltingpoint line of the system of the two substances (the aldehyde melts at 45° , the acid is decomposed at about 200°) the point up to which they are still capable of forming mixed crystals may perhaps be determined more accurately. It is not improbable that in the intramolecular rearrangements of other solid substances solid solutions may also be formed; if possible this will be further investigated.

Chemistry. — “*The transformation of diphenyliodonium iodide and chloride and its velocity*”. By Mr. E. H. BÜCHNER. (Communicated by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the meeting of March 28 1903).

It is about 10 years ago that VICTOR MEYER and HARTMANN¹⁾ announced the important discovery of a new class of iodine derivatives, the iodonium bases, substances with a trivalent iodine atom, having about the same basic power as the ordinary alkalis and capable of forming salts. The simplest representative of this interesting class of substances is diphenyliodonium-hydroxide: $(C_6H_5)_2 J OH$; the salts, such as the chloride or the nitrate, when dissolved in water, appeared to possess a conductive power corresponding with that of the alkali salts²⁾.

The behaviour of the halogen salts of the base, when heated, is peculiar; VICTOR MEYER and HARTMANN noticed that on fusing these salts at 175° a decomposition sets in, which spontaneously leads to a complete conversion into halogen-benzene $(C_6H_5)_2 = J-J = 2 C_6H_5J$ with strong evolution of heat.

This transformation now deserved a closer study. It may be considered as a depolymerisation but is distinguished however from many other similar reactions, not only by the great difference in character between the decomposing substance and the products of decomposition but also by the fact that the transformation is not reversible. At all events, up to the present no process is known which leads straight from iodobenzene to diphenyliodoniumiodide. In this latter respect the above mentioned reaction is distinguished from the transformation with which it has been compared namely that which tetramethylammonium iodide suffers on heating; the latter substance is readily prepared from its products of decomposition at the ordinary temperature.

¹⁾ Ber. **27**. 502, 1594. (1894).

²⁾ SULLIVAN Z. ph. Ch. **28**. 523. The salts are, therefore, not dissociated hydrolytically.

It was to be expected that the decomposition of the diphenyliodonium-salt would take place at temperatures considerably below the melting-point, and this is actually the case.

1. Beforehand, however, it was deemed desirable to study the behaviour of the iodide towards light as in the study of the velocity of transformation account had to be taken of a possibly existing sensitiveness to light ¹⁾).

I have found that in the case of the iodide the transformation is caused by exposure to light ²⁾); whilst it remains quite intact when kept in the dark for 2¹/₂ months. It was to be expected that the source of the light would affect the transformation. The following results were obtained:

Electric Arc-Light:	after 1	hour titre:	26.6%	J,	converted	about	14.5%
"	"	"	1 ¹ / ₂	"	"	"	20
Sunlight:	"	4	"	"	30.0	"	3.5
"	"	30	"	"	13.0	"	60
Auer Light:	"	170	"	"	29.1	"	6.4
Diffuse Daylight:	a.	10 weeks:	24.7	"	"	"	20.5
"	b.	"	20.3	"	"	"	35

The decomposition of the iodide is therefore most rapidly effected by the arc-light.

2. If now the solid iodide was exposed to temperatures considerably below its meltingpoint a more or less slow conversion seemed to take place. Whereas 1% at most was decomposed at 90° after 3 hours, about 36% had disappeared at 100° after 13 hours, whilst after heating at 123° for 3¹/₂ hours only 5% was left undecomposed. This shows that the decomposition of the solid substance already takes place even at temperatures considerably below the meltingpoint. This also applies to the solid chloride which however is more stable than the iodide.

Several series of experiments were now made with the solid iodide

¹⁾ The quantitative estimation of iodonium haloid and halogen-benzene in the presence of each other is simply done by titration with AgNO₃; the first when introduced into water yields one of the halogen atoms as ion whilst iodo- or chlorobenzene does not react with AgNO₃.

For diphenyliodonium-iodide was found: according to CARUS 62.1 and 62.1% J, calculated 62.2%; by titration 31.0 and 31.1% J. The chloride gave on titration 11.15% Cl, calculated 11.2%.

²⁾ V. MEYER states that it turns yellow on exposure to light.

at temperatures of 105—110°; the results obtained will be communicated on a future occasion.

3. It was obvious that I should try to make a closer study of the velocity of transformation of the iodide in solution. Its great insolubility, however, rendered the operation impossible; of the many solvents which were tried, pyridine proved to be the best; the solubility of the iodide was however still too small, namely only about $1\frac{1}{2}$ ‰.

The more soluble diphenyliodonium-chloride was better suited for the purpose; the solubility in water, although not large, proved sufficient at the temperature at which the operation took place (98—99°).

The results obtained in fifteen velocity determinations were at first very unsatisfactory and pointed to the existence of many interfering influences. The coefficients obtained on applying the formulæ for unimolecular and bimolecular reactions were anything but constant and often pointed to a very irregular course. In one experiment coefficients were obtained which were many times greater than those got in another apparently quite analogous case. Sometimes the coefficients diminished equally, sometimes the reaction after proceeding for a while, suddenly ceased. After many similar negative results it at last appeared that the conversion of diphenyliodonium-chloride into chloro- and iodobenzene is influenced to an extraordinary degree by the presence of very small quantities of impurities. Very small quantities of acid retard the reaction to a remarkable extent or bring it to a standstill: the presence of traces of iodine causes a regular fall in the reaction coefficient; a little of the free base (diphenyliodonium-hydroxide) accelerates, on the other hand, the decomposition in a strong degree. The halogenbenzenes formed during the reaction appeared however to be inert.

On now using a very pure preparation free from acidity and of a pure white colour and applying the formula for reactions of the second order, coefficients were obtained which could be considered as constants. (see table p. 649).

On adding 6 cc. of $\frac{n}{25}$ HCl, the coefficient (which, moreover, was not constant) fell to about half the value obtained in experiment I while the presence of 8 cc. of $\frac{n}{25}$ $(C_6H_5)_2$ JOH increased the coefficient about $\frac{1}{4}$ or 5 times ¹⁾.

¹⁾ The following experiment also may show how sensitive the transformation is to very trifling quantities of foreign substances. To a solution of the chloride ($C_0 = \frac{1}{20.2}$, $T = 99.0$), which after $3\frac{1}{2}$ hours had fallen from 30.67 AgNO₃ to 23.71, was added 39.3 milligr. of a well crystallised chloride which was coloured

I. T = 99°.4 C ₀ = 1/27.2 ¹⁾ 2.909 gr. in 250 cm ³ .			
t in hours.	ccm. AgNO ₃	K ₁	K ₂
0	22.96		
18	12.25	0.0152	4.32
20	11.87	143	4.27
22	11.42	143	4.31
24	10.87	135	4.26
25	10.50	136	4.29
28	9.94	130	4.27
30	9.42	129	4.30

II. T = 99.4 C ₀ = 1/16.8			
t	AgNO ₃	K ₁	K ₂
0	37.47		
1 1/2	33.82	0.0273	4.44
4 1/4	27.85	295	4.32
9	22.72	236	4.49
9 3/4	22.25	229	4.16

III. T = 99.0 C ₀ = 1/22.6 trace of iodine added.		
t	AgNO ₃	K ₂
0	27.75	
1 1/2 h.	25.37	4.43
3 1/2	23.00	4.33
5 1/2	22.00	4.40
11 1/2	18.37	4.00
23 1/2	15.77	0.88

IV. T = 99.4 C ₀ = 1/22.7 25 cm ³ 1/25 HCl added to 150 cm ³ . Conc. of the HCl therefore 1/175 n.	
t	AgNO ₃
0	27.50
2 h.	27.50
4	27.42
22	26.61
neutral. with NaOH	
26	21.32
28	17.87

If, by means of the VAN 'T HOFF formula²⁾, we calculate the order of the reaction from the communicated experiments and also from a few which are not yet communicated, we find $n = 2.1, 1.9$ and 2.1 . From this, and also from the fact that in experiment I the K_2 's are constants, it follows that the transformation

somewhat yellow, but gave on analysis the theoretical number for chlorine. By this addition the titre naturally increased and came to 26.10; 2 1/2 hours later the solution did not appear to have changed (found 26.08). The somewhat coloured chloride was found to have a faint acid reaction and to give blue colour with starch solution after some time.

1) K_1 is calculated according to the formula for reactions of the first, K_2 according to that for reactions of the second order.

2) Vorlesungen, I. 193.



is a bimolecular one.

Since the chloride is comparable with a salt such as KCl, it may be concluded that the transformation does not occur in the non-dissociated molecules but between the ions. This idea would agree with that propounded by WALKER and HAMBLY¹⁾ for the transformation of ammonium isocyanate in aqueous or alcoholic solution into urea, a reaction which also appeared to be a bimolecular one. WALKER and HAMBLY were enabled to support their view by showing that either ammonium- or isocyanic acid ions cause a retarding influence on the reaction investigated by them as both diminish the dissociation of ammonium isocyanate. In our case a similar behaviour of chlorine and iodonium atoms does not present itself. Hydrochloric acid has certainly a retarding influence but this is too large to be explained by a diminution of the ionisation. Then again, iodonium hydroxide has a strong accelerating power. We must, therefore, think here of a special catalyzing influence of hydrogen- and hydroxyl ions: apparently the first acts here as a retarding catalyzer, an influence of which up to the present but few instances are known. Then, if the acid is neutralised (compare expmt. IV), the transformation proceeds in a regular manner whilst the chlorine ion is still present in about the same concentration.

The most probable view of the mechanism of the transformation of the iodonium haloids is therefore that the reaction takes place between two molecules.

A trace of iodine retards the transformation in an increasing degree. This investigation will be continued later on.

Organic. chem. Laboratory, University of Amsterdam.

Chemistry. — “*Nitration of symmetrical dinitroanisol.*” By Dr. J. J. BLANKSMA. (Communicated by Prof. C. A. LOBRY DE BRUYN).

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

In a previous communication²⁾ it has been stated that pentanitrophenol is readily formed by the action of nitric acid on symmetrical dinitrophenol whilst symmetrical dinitroanisol is attacked with difficulty by nitric acid. It seemed, however, not impossible that symmetrical dinitroanisol might still be further nitrated and this indeed appeared

¹⁾ J. Ch. Soc. **67**. 746 (1895).

²⁾ Proc. Royal Acad. 25 Jan. 1902.

to be the case. If symmetrical dinitroanisol is treated for two hours on the waterbath with a mixture of HNO_3 (density 1.44) and sulphuric acid, trinitroanisol is formed m. p. 104° . The nitrogroup introduced into this substance is mobile and easily replaced by OH , OCH_3 , NH_2 , NHCH_3 etc. If the NO_2 group is replaced by OH dinitroguaiacol is formed m.p. 121° . By treatment with alcoholic methylamine, methyl-amido-dinitroanisol is formed m.p. 168° , which is converted by nitric acid of 1.52 sp. gr. into oxymethyl-dinitrophenyl-methylnitramine m.p. 118° already obtained by GRIMAUD and LEFÈVRE ¹⁾ by nitration of dimethyl-orthoanisidine. This goes to prove that the nitrogroup in regard to the OCH_3 -group has been introduced into the ortho place and that, therefore, the constitution of trinitroanisol is represented by $\text{C}_6\text{H}_2\text{OCH}_3(\text{NO}_2)_3$. 1. 2. 3. 5.

If trinitroanisol is treated with a solution of NaOCH_3 in methyl alcohol the NO_2 group 2 is replaced by OCH_3 and the dimethylether of dinitropyrocatechine is formed, m.p. 101° . Treatment with alcoholic ammonia yields dinitroanisidine $\text{C}_6\text{H}_2(\text{OCH}_3)\text{NH}_2(\text{NO}_2)_2$ 1. 2. 3. 5, m. p. 174° ; with aniline and aethylamine are formed compounds melting respectively at 155° and 123° .

If trinitroanisol is nitrated with a mixture of nitric acid of 1.52 sp. gr. and sulphuric acid a tetranitroanisol is formed m.p. 154° . On treatment with 2 mols. of NaOCH_3 , this substance is converted into crystals which melt at 165° and assume a purple-brown color when exposed to light.

Analysis shows that two NO_2 groups are replaced by OCH_3 . LORING JACKSON ²⁾ by treating symmetrical tribromodinitrobenzene with 3 mols. of NaOCH_3 has prepared a compound with the same properties as the above mentioned; he however considered that he had obtained the dimethylether of dinitroresorcinol. The latter substance melts however, according to FREYSS ³⁾ and MELDOLA ⁴⁾ at 154° , whilst MEERUM TERWOGT ⁵⁾ and I have found 157° . It is therefore very probable that LORING JACKSON has been dealing with the trimethylether of dinitrochloroglucinol as, on treating symmetrical tribromodinitrobenzene with NaOC_2H_5 , all three Br-atoms may be replaced by OC_2H_5 ⁶⁾.

That the compound obtained from tetranitroanisol and NaOCH_3 is really identical with that from symmetrical tribromodinitrobenzene

1) Compt. Rend. **112**. 727.

2) Amer. Chem. Journ. **13**. 180.

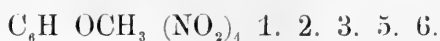
3) Centr. Blatt. 1901. I. 739.

4) Proc. Chem. Soc. **17**. 131.

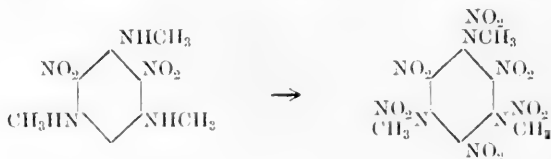
5) Rec. **21**. 288.

6) Amer. Chem. Journ. **21**. 512.

was shown by taking the meltingpoint of a mixture of the two substances; no lowering of the meltingpoint was noticed. It is therefore proved that from tetranitroanisol and NaOCH_3 the trimethyl-ether of dinitrophenoroglucinol is obtained and consequently the constitution of the tetranitroanisol is:



If symmetrical tribromodinitrobenzene is treated in alcoholic solution with six mols. of methylamine, the three bromine atoms are readily replaced by NHCH_3 and we obtain fine orange-red needles m.p. 220° (with decomposition). When this symmetrical $\text{C}_6\text{H}(\text{NO}_2)_2 (\text{NHCH}_3)_3$ is dissolved in nitric acid of 1.52 sp. gr. and then diluted with water a fine white crystalline powder is obtained which, when dissolved in glacial acetic acid, deposits small beautiful white needles, which explode between 200° and 203° , sometimes causing a flame. From the analysis it appears that this is the symmetrical trinitrophenyltrimethyltrinitramine.



Geology. — “*Two New Mid-Cambrian Erratic-Blocks from the Dutch Diluvium*”. By J. H. BONNEMA at Leeuwarden. (Communicated by Prof. J. W. MOLL).

I. When I had been appointed assistant at the Geological-Mineralogic Institute at Groningen, I was charged with the task of determining the fossils that are found in the collection of Groningen sedimentary erratic-blocks. If we succeed in this with a fossil, we can as a rule more or less accurately, for the erratic-block in which it occurs, fix the age of the layer of which it formerly formed part; at the same time it may be found out whether suchlike stone is still known as firm rock, — and whether the same kinds of erratic-blocks have been met with in any other places.

With many pieces I succeeded, but with a not inconsiderable number I failed, owing to various causes. To the latter division belonged i. a. two small pieces of lime-stone, the largest dimensions

of which are about 4 centimetres. They originally made part of one erratic-block, which was found when the ramparts near one of the former Groningen gates (Boteringepoort) were dug off. One of the pieces still shows a part of the original surface possessing distinct glacierscratches.

From the pieces preserved it may be concluded that this erratic-block consisted of green-grey, rather compact, marly lime-stone, in which with a magnifying glass many little grey grains and here and there little dark-green lustrous Glauconite-grains may be distinguished. I observed one single Pyrite-crystal. At the surface it had, to a depth of about 1 centimetre, become more or less yellow, under the influence of corrosion.

The part preserved also shows that through this erratic-block ran a layer that was rich in Trilobites-remains. For the greater part the transverse sections of them are visible. In one piece, however, some remains are partly or entirely exposed to view. A mid-shell is the most important of them.

This mid-shell, across which run various flaws, and which consequently is not likely to have entirely retained its original shape, is lengthwise rather strongly vaulted and has a length of 12 millimetres, its breadth amounting to about 14 millimetres. It is almost everywhere the same, the lines that connect the beginning and the termination of the facial suture, running almost parallel to the longitudinal axis. The front-edge is regularly curved. The occipital-furrow is shallow, especially on the glabella. The length of the rather broad glabella is about $\frac{3}{4}$ of that of the mid-shell. It is tongue-shaped and bounded by shallow dorsal furrows. The latter first run nearly parallel to each other and then turn to the centre, where they meet. Lateral furrows are not to be distinguished on the glabella. That part of the mid-shell which lies in front of the glabella, slants down rather quickly. The parts on either side slant down more slowly.

As to the sculpture, along the front-edge of the mid-shell, parallel to it, run fine stripes. The shell moreover shows all over, very near each other, fine pricked points. The colour of the shell is partly black, partly yellow-grey (cream-coloured).

In spite of repeated efforts I had never before succeeded in discovering what species of Trilobites this mid-shell came from. This summer, however, I was more fortunate. On my journey to Oeland it chanced that near the hospital at Borgholm a pit was being dug and that, while doing this, people had penetrated as far as the layer with *Paradoxides Oelandicus* Sjögren. The stone that had been produced from the pit, was still present. It consisted of greenish marl-slate,

which had entirely fallen asunder, and of rather large lime-concretions. This clashes with LINNARSSON'S¹⁾ opinion, that at Borgholm this layer should consist of marl-slate only, which opinion was afterward made use of by ROEMER²⁾ and REMELÉ³⁾.

In the said lime-concretions I found, besides some remains of *Paradoxides Oelandicus* Sjögren and a couple of nearly complete specimens of *Ellipsocephalus Polytomus* LINNARSSON, countless mid-shells of the latter species of Trilobites.

Here was confirmed the opinion of LINNARSSON⁴⁾ that the absence of stripes on the front-edge of the mid-shells, and that of the pricked points, on the scale of the *Ellipsocephalus*-species occurring at Borgholm, by which this species was said especially to differ from the Stora Frö-species, must be attributed to the circumstance that his Borgholm material came from marl-slate, and that of Stora Frö from lime-stone. The stripes and the pricked points are remarkably distinct in the mid-shells I gathered from the lime-concretions at Borgholm. Consequently there is no reason any more for not ranging the *Ellipsocephalus*-remains of Stora Frö under the head: *Ellipsocephalus Polytomus* LINNARSSON, the difference in size only not sufficing to maintain the contrary.

One of the lime-concretions contained a layer that was peculiarly rich in mid-shells of *Ellipsocephalus Polytomus*. While breaking this concretion to pieces, I was immediately reminded of my Groningen erratic-block; and now that I have compared the latter with the pieces I brought from Borgholm, I know that they are exactly alike. In both the stone is the same, except that the Groningen piece has a yellow tint, which must be attributed to the influence of corrosion. The mid-shells of *Ellipsocephalus Polytomus*, occurring in both, also resemble each other, in colour as well as in their numerous flaws.

Consequently it may with perfect certainty be declared that the erratic-block mentioned above has the same age as the layer with *Paradoxides Oelandicus* Sjögren (the oldest of the Mid-Cambrian), and that a corresponding kind of stone is still found at Borgholm in Oeland. It is probably also met with at Stora Frö in the same island. I cannot say so for certain, however, as I did not go there and so do not possess any limestone from that place, which might be used for comparison.

1) LINNARSSON. Om Faunan i lagren med *Paradoxides Oelandicus*. Geol. Förenings i Stockholm Förhandlingar. Bd. 3. pag. 354.

2) ROEMER. *Lethaea erratica*. pag. 37.

3) REMELÉ. Zeitschr. d. deutsch. geol. Gesellschaft. Bd. 33. 1881, pag. 183, 701.

4) LINNARSSON. Loc. cit. pag. 364.

This is the first time that mention is made of such an erratic-block from the Dutch diluvium. Many of the kind, with remains of *Ellipsocephalus Polytomus* or of other fossils, occurring in Oeland in the layer with *Paradoxides Oelandicus*, have already been found in the German diluvium. The first of them was mentioned by DAMES¹⁾ and comes from Rixdorf near Berlin. A few years after, REMELÉ²⁾ described two such erratic-blocks from the neighbourhood of Eberswalde. Later on, ROEMER³⁾ made mention of two erratic-blocks of the same age. One of them comes from Rostock and bears much resemblance, according to the description, to the Groningen piece. This cannot with so much certainty be said of the second block, which was found at Bromberg and does not seem to be greenish. In Sleswick-Holstein, too, corresponding erratic-blocks seem to have been found, as STOLLEY⁴⁾ writes about „grünliche Kalkgeschiebe der Oelandicus-Zone”.

This erratic-block also confirms my supposition formerly⁵⁾ mentioned, that in the Hondsrug occur more sedimentary erratic-blocks with a West-Baltic character, than was formerly generally supposed.

II. For some time already I have had in my collection several pieces of an erratic-block consisting of limestone that has been tinted dark-grey, even almost black, by bitumen. It was found in the loam-pit near Hemelum. Its calcium-carbonate having for the greater part crystallized, this limestone approaches antraconite. Some nests of little pyrite-crystals and a small phosphorite-nodule are found in the stone.

For a long time the only fossil that was exposed to sight was (with the exception of a few unimportant remains, probably of a *Paradoxides*) what I supposed to be the internal cast of the inside of a piece of Trilobite-shell. Its largest dimension amounts to 9 millimetres. This internal cast is almost oval, and strongly vaulted. The top-part finishes in a bow. On the convex side of this bow it is steeper than on the concave one. In front, on the least steep part, is a frame in relief, soon turning round the most elevated point and then continuing on the steepest part, where it becomes tinier and tinier. Towards either side springs from this frame a net-work of

1) DAMES, Zeitschr. d. deutsch. geol. Gesellschaft. Bd. 31. 1879. pag. 795.

2) REMELÉ, Zeitschr. d. deutsch. geol. Gesellschaft. Bd. 33, 1881. pag. 181, 700.

3) ROEMER, *Lethaea erratica*, pag. 26.

4) STOLLEY, *Die Cambrischen und Silurischen Geschiebe Schleswig-Holsteins und der benachbarten Gebiete*, 1895. Bd. I, Heft 1, pag. 40.

5) BONNEMA. “Cambrian erratic-blocs at HEMELUM in the South-west of Frisia.” *These Proc.* 1902, p. 142.

suchlike ones. This net-work is very distinct on the less steep part, not so distinct on the other, where it is scarcely to be seen with a magnifying glass. Moreover there are on this internal east round elevations.

It being quite impossible for me to find what species of Trilobites this off-print came from, the exact age of this erratic-block could not be fixed. The nature of the stone made it likely to be Cambrian, and that, too, Mid-Cambrian, because of the suppositional *Paradoxides*-remains.

When, however, a few weeks ago, my friend dr. GRÖNWALL from Copenhagen, the author of "*Bornholms Paradoxideslag og deres Fauna*" (Danmarks geologiske Undersøgelse II Række No. 13.) took a view of my collection of erratic-blocks, he recognized in the said off-print that of a right cheek of *Conocoryphe Exsulans* Linnr.¹⁾ Herewith the age of this erratic-block was already exactly determined, for the occurrence of these Trilobites-remains is characteristic of the lower part of the layers with *Paradoxides Tessini* Brongn.

This division consists, in Schonen, in Bornholm and (according to an oral communication of prof. MOBERG) to the South of Mörbylånga in Oeland, of limestone, which after this Trilobite is at present mostly called *Exsulans*-limestone, whilst it ceased to be called *Coronatus*-limestone.

GRÖNWALL'S opinion was brilliantly confirmed, when, on his breaking the stone further to pieces, remains of the Trilobites *Conocoryphe Impressa* Linnr.²⁾ *Liostracus Aculeatus* Ang.³⁾ and *Solenopleura Parva* Linnr.⁴⁾ were exposed to view by him. Moreover a remnant of *Aceroteta Socialis* v. Seebach was found, which, however, also occurs in older and in younger layers, which is not the case with the Trilobites mentioned just now.

The only remnant that has been well preserved, is a mid-shell of *Conocoryphe Impressa* Linnr. It is for the greater part exposed to view. Only on the sides it is still covered by the stone; so the facial sutures are invisible. It must have belonged to a young individual, its length being only 6 millimetres. It is slightly vaulted, the glabella a little more than the other part. In front it is bounded by a flat border along the edge, which border is broadest in the middle.

1) LINNARSSON. Om. Faunan i Kalken med *Conocoryphe exsulans* (*Coronatus*-Kalken). Sveriges geologiska Undersökning. 1879. Ser. C. No. 35. pag. 15. tafl. II, fig. 21, 22.

2) LINNARSSON. loc. cit. pag. 20. tafl. II. fig. 29, 30.

3) LINNARSSON. loc. cit. pag. 11. tafl. I. fig. 12—15.

4) LINNARSSON. loc. cit. pag. 14. tafl. I. fig. 16—19, 20?

The occipital furrow is shallow, especially on the glabella. The neck-ring broadens towards the centre and bears a little tubercle there. The breadth of the glabella is at the back equal to its length, which is half the breadth of the mid-shell. The glabella becomes gradually narrower towards the front; in front it is rounded. On either side there are three very indistinct lateral furrows. The dorsal furrows are little developed. In front of the glabella the cheeks run almost imperceptibly into each other. On either side an oblong elevation is visible on the firm cheek, just behind the place where the dorsal furrow turns down towards the centre. It is scarcely to be observed that starting from this elevation a line-shaped one runs in the direction of the corners of the cephalon, as LINNARSSON tells us. This must certainly be attributed to the circumstance, that this mid-shell belonged to a young individual. The scale possesses no other sculpture than countless very fine impressed points, placed very close to each other.

From the properties mentioned above one may easily convince oneself that the mid-shell described comes from *Conocoryphe impressa* Linn., and that consequently this erratic-block is a piece of Exsulans-limestone.

The other Trilobites-remains, all of them pieces of mid-shells, are too incomplete to be described in such a manner, that the species of Trilobites which they come from might be recognized from the description. Moreover, such a description would be more or less superfluous, as the age of this erratic-block has already been sufficiently indicated. So I think I'd better leave it and refer to the authority of Dr. GRÖNWALL with regard to the remains of the other Trilobites mentioned. As he was so kind as to send me some mid-shells of these Trilobites for comparison, I could convince myself of the correctness of his determinations.

As was mentioned above, Exsulans-lime is found as firm rock in Bornholm, in Schonen, and southward of Mörbylånga in Oeland. Mörbylånga does not seem to have been mentioned yet in literature in this connection; but Prof. MÖBERG told me of it. In Schonen, Exsulans-lime is without any doubt met with as firm rock near Andrarum, Gislöf and Kwiks Esperöd. Most probably it is also found as such, according to LINNARSSON, near Fågelsång in the neighbourhood of Lund.

GRÖNWALL tells me that my erratic-block does not, petrographically, correspond with the Bornholm Exsulans-lime, more with that in South-East Schonen. I cannot decide whether it also resembles that which is found at Mörbylånga in Oeland.

In the Dutch diluvium an erratic-block of this kind was never

before found. They also seem to be very rare in the German diluvium. As far as I have been able to find out, they are made mention of by STOLLEY ¹⁾ only.

Mathematics. — “*An analytical expression for the greatest common divisor of two integers.*” By Prof. J. C. KLUYVER.

In this paper we propose to construct certain functions z of two real variables x and y which for positive and integer values of these variables become equal to the greatest common divisor of x and y .

A very simple solution of this problem is obtained as follows. Denote by $[u]$ the integer part of the number u and consider the arithmetical discontinuous function

$$P(u) = u - [u] - \frac{1}{2}.$$

For any integer n we have

$$P(u + n) = P(u), \quad P(u + 0) = -\frac{1}{2}, \quad P(u - 0) = +\frac{1}{2}.$$

We will take

$$P(n) = P(n - 0) = +\frac{1}{2}$$

and consequently

$$[n] = [n - 0] = n - 1.$$

Integer values of u excepted the wellknown relation

$$P(u) = -\frac{1}{2} \sum_{n=1}^{n=\infty} \frac{\sin 2 \pi n u}{2 \pi n}$$

holds and from it we deduce the identical equation

$$\sum_{\mu=0}^{\mu=\alpha-1} P\left(u + \frac{\mu}{\alpha}\right) = \sum_{\mu=0}^{\mu=\alpha-1} P\left(u + \frac{\mu\beta}{\alpha}\right) = P(\alpha u),$$

where α and β are relative prime integers. That the identity is still valid for integer values of u may be easily verified.

By the equation

$$z = 2 \sum_{\mu=0}^{\mu=[x]} P\left(\frac{\mu y}{x}\right) (1)$$

a discontinuous function of the variables x and y is defined. We may regard it as a first solution of the proposed problem. For if

¹⁾ STOLLEY. loc. cit. p. 41.

x and y become integers, say $x = \alpha D$, $y = \beta D$, where α and β are prime to each other, we have

$$z = 2 \sum_{\mu=0}^{\mu=\alpha D-1} P\left(\frac{\mu y}{x}\right) = 2 D \sum_{\mu=0}^{\mu=\alpha-1} P\left(\frac{\mu}{\alpha}\right) = 2 D P(0) = D.$$

In a somewhat different form this result is found in a paper by STERN¹⁾. A whole set of functions of the required kind may be deduced in quite the same way. We only have to notice that the function

$$F'_s(u) = \sum_{n=1}^{n=\infty} \frac{\cos 2 \pi n u}{n^s}, \quad (s > 1)$$

satisfies the fundamental relation

$$\sum_{\mu=0}^{\mu=\alpha-1} F'_s\left(u + \frac{\mu}{\alpha}\right) = \sum_{\mu=0}^{\mu=\beta-1} F'_s\left(u + \frac{\mu\beta}{\alpha}\right) = \alpha^{1-s} F'_s(\alpha u),$$

where again α and β are prime to each other.

Hence if we put

$$F'_s(0) z^s = x^{s-1} \sum_{\mu=0}^{\mu=\lceil x \rceil} F'_s\left(\frac{\mu y}{x}\right), \quad \dots \dots \dots \text{(II)}$$

we get for $x = \alpha D$, $y = \beta D$

$$F'_s(0) z^s = \alpha^{s-1} D^{s-1} \sum_{\mu=0}^{\mu=\alpha D-1} F'_s\left(\frac{\mu\beta}{\alpha}\right) = \alpha^{s-1} D^s \sum_{\mu=0}^{\mu=\alpha-1} F'_s\left(\frac{\mu\beta}{\alpha}\right) = D_s F'_s(0),$$

that is

$$z = D.$$

In the functional relation (II) the term $F'_s\left(\frac{\mu y}{x}\right)$ is not easily evaluated; hence the series $F'_s(u)$ may be suitably replaced by the latter of the two series

$$g_{2k-1}(u) = 2 (-1)^k \sum_{n=1}^{n=\infty} \frac{\sin 2 \pi n u}{(2 \pi n)^{2k-1}},$$

$$g_{2k}(u) = 2 (-1)^{k-1} \sum_{n=1}^{n=\infty} \frac{\cos 2 \pi n u}{(2 \pi n)^{2k}}.$$

Indeed, if we denote the Bernoullian polynomial of order m

$$\frac{u^{m+1}}{(m+1)!} - \frac{1}{2} \cdot \frac{u^m}{m!} + \frac{B_1}{2!} \cdot \frac{u^{m-1}}{(m-1)!} - \frac{B_2}{4!} \cdot \frac{u^{m-3}}{(m-3)!} + \dots \dots \dots,$$

by $f'_m(u)$ the series $g_m(u)$ is identical with $f'_m(u)$ for all values of u between zero and unity. Therefore, whatever may be u , the series $g_m(u)$ may be regarded as a polynomial of the m^{th} degree in

¹⁾ "Zur Theorie der Function $E(x)$," Journal f. Math., 102, p. 9.

$u = [u]$ so that, if in the equation (II) we replace $F_s(u)$ by $g_{2k}(u)$,

$$(-1)^{k-1} \frac{B_k}{2k!} z^{2k} = x^{2k-1} \sum_{\mu=0}^{x=[x]} g_{2k}\left(\frac{\mu y}{x}\right), \dots \dots \dots \text{(III)}$$

the thus defined function z is algebraically expressed in x and y . But as well as in the equations (I) and (II) z is still discontinuous for integer values of x in equation (III). By a slight alteration it is possible to make these discontinuities disappear. Without altering the value of z for integer values of x and y we may write instead of (III)

$$(-1)^{k-1} \frac{B_k}{2k!} z^{2k} = x^{2k-1} \left\{ \sum_{\mu=1}^{x=[x]} g_{2k}\left(\frac{\mu y}{x}\right) + \frac{1}{2} g_{2k}(0) + g_{2k}(y) P(x) \right\} \dots \text{(IV)}$$

and the function z has become continuous everywhere. The same however is not true for the partial derivatives of z with respect to x or y ; besides there is as in equations (I) and (II) a lack of symmetry. By interchanging x and y the value of z alters. To some extent these disadvantages may be eliminated. The process of integration is apt to level finite discontinuities, moreover symmetry may be introduced by it. And indeed a suitable expression of z in the form of a definite integral can be given.

We consider the function z defined by

$$\frac{B_k}{2k!} z^{2k} = x^k y^k \int_0^1 g_k(xu) g_k(yu) du \dots \dots \dots \text{(V)}$$

Now z depends symmetrically on x and y and is continuous throughout. The function has continuous derivatives; we may differentiate z a number of $k-1$ times with respect to x and also $k-1$ times with respect to y , either separately or subsequently, before the derivatives lose their continuity, so that by making k larger and larger the behaviour of z tends more and more to that of an analytical function of two real variables.

We now again substitute in (V) $x = \alpha D$, $y = \beta D$ and as the trigonometrical series $g_k(xu)$ and $g_k(yu)$ are absolutely convergent (under the supposition $k > 1$) we may multiply termwise and integrate the partial products.

But after integration a nonvanishing amount is furnished only by those partial products

$$\frac{\sin 2\pi h \alpha D u}{\cos} \quad \frac{\sin 2\pi l \beta D u}{\cos}$$

in which we have

$$h = g\beta \quad , \quad l = g\alpha;$$

hence we find

$$\frac{B_k}{2k!} z^{2k} = \frac{4D^{2k}}{(2\pi)^{2k}} \cdot \frac{1}{2} \sum_{g=1}^{g=\infty} \frac{1}{g^{2k}} = \frac{B_k}{2k!} D^{2k}$$

and as before

$$z = D.$$

Had we integrated the product $g_m(xu) g_n(yu)$, where $m + n$ is even, instead of $g_m(xu) g_m(yu)$ the result would have been similar, only symmetry would have been lost.

We may remark that the z in equation (V) is still an algebraical function. For remembering that

$$\frac{d}{du} g_k(u) = g_{k-1}(u),$$

$$g_1(u) = P(u),$$

we deduce by repeated partial integration

$$\begin{aligned} \frac{B_k}{2k!} z^{2k} &= \sum_{\nu=0}^{\nu=k-2} (-1)^\nu x^{k+\nu} y^{k-1-\nu} g_{k-\nu}(x) g_{k+\nu+1}(y) + \\ &+ (-1)^{k-1} x^{2k-1} \left\{ g_1(xu) g_{2k}(yu) \right\}_{u=0}^{u=1} + (-1)^k \frac{x^{2k}}{y} g_{2k+1}(y), \end{aligned}$$

or finally

$$\begin{aligned} \frac{B_k}{2k!} z^{2k} &= \sum_{\nu=0}^{\nu=k-2} (-1)^\nu x^{k+\nu} y^{k-1-\nu} g_{k-\nu}(x) g_{k+\nu+1}(y) + \\ &+ (-1)^k \frac{x^{2k}}{y} g_{2k+1}(y) + \\ &+ (-1)^{k-1} x^{2k-1} \left\{ \sum_{\mu=1}^{\mu=\lceil x \rceil} g_{2k} \left(\frac{\mu y}{x} \right) + \frac{1}{2} g_{2k}(0) + g_{2k}(y) P(x) \right\}. \quad \text{(VI)} \end{aligned}$$

From this equation we infer that the product $z^{2k}xy$ is a rational integral function of x and y of degree $4k + 2$, and generally speaking the equation represents an algebraical surface S of that degree. But it should be noticed that this surface S in reality is composed of an infinite number of partial surfaces, having contact more or less close along a system of plane curves C . And in fact the larger the integer k be chosen the closer will be the contact of the partial surfaces. Equation (VI) contains the equations of all the partial surfaces, but each of them has a distinct equation the coefficients of which are made up from the integers

$$[x], [y] \text{ and } \left[\frac{\mu y}{x} \right], \quad (\mu = 1, 2, 3, \dots [x]).$$

Hence we pass from one partial surface to an adjacent one in all places, where one at least of these integers increases by unity.

Thus the projections on the xy -plane of the curves C are of two distinct categories. To the first belong the straight lines $x=n$, $y=n$, regularly dividing the xy -plane in equal squares of side unity. The second category is formed by straight lines issuing from the vertices of these squares and which, if produced, would pass through the origin. The number of these lines, which have their points of issue inside the square, bounded by the x -axis, the y -axis and by the lines $x=n$, $y=n$ is seen to be $2\sum\varphi(n)^1$, that is on an average equal to $\frac{6}{\pi}n^2$. Therefore the partial surfaces remote from the origin ultimately take the form of infinitely narrow strips, the length of which varies from 1 to $\sqrt{2}$.

In order to lower as far as possible the degree of the surface S , we should take $k=1$ and we have from (V) and (VI)

$$\frac{1}{12}z^2 = xy \int_0^1 P(xu)P(yu)du = x \left\{ \sum_{u=1}^{u=[x]} g_2\left(\frac{uy}{x}\right) + \frac{1}{2}g_2(0) + g_2(y)P(x) \right\} - \frac{x^2}{y}g_3(y).$$

A comparison with (IV) makes it evident that for integer values of x and y the quantity z still becomes equal to the greatest common divisor. The surface S is of the 6th degree, the partial surfaces still hang together everywhere but in this case they have no contact along the curves C .

Physics. — “*On maxima and minima of intensity sometimes observed within the shading of strongly widened spectral lines.*”²⁾
By Prof. W. H. JULIUS.

While examining a series of photographs of the solar spectrum, made by ROWLAND in 1888 and 1889, JEWELL discovered one plate on which the shading of H and K was broken up into a system of faint, nebulous lines, symmetrically arranged about the central absorption lines³⁾. The distances apart of the component lines of the series increased as the distance from the central line increased. On some other photographs of the solar spectrum, taken by ROWLAND and by himself, he only found feeble indications of these series; but

¹⁾ $\varphi(n)$ denotes the number of integers less than n and prime to n .

²⁾ Part of the contents of this communication has already been shortly mentioned in a foot-note which was added to the English translation of a former paper (Proc. Roy. Acad. Amst. IV, p. 601) but did not occur in the Dutch original of the same.

³⁾ L. E. JEWELL, *Astrophysical Journal*, III. p. 108, 1896, and VIII, p. 51—53, 1898.

in the shading of some of the strongest lines of iron and a few other elements a similar structure was observed, the component lines being faint, nebulous, and close together.

The plate which showed the structure of *H* and *K* most plainly, displayed an additional peculiarity, as on it the general shading of those lines was unusually weak.

In HALE'S abnormal spectrum¹⁾, which was characterized by the extreme weakness of the shaded background of many absorption lines, maxima and minima of intensity were also distinguishable under a microscope, though they did not appear so clear nor so regularly arranged as in the case described by JEWELL.

If we suppose the principal cause of the shading of the Fraunhofer lines not to be the absorption, but rather the anomalous dispersion of the waves, which in the spectrum are situated on either side the central absorption line²⁾, we can easily account for the phenomenon, before mentioned, as well as for the fact, that in very rare cases only it shows distinctly.

Let us consider a narrow beam of light of an exactly defined wave-length, belonging to the shaded background of a Fraunhofer line. This beam has emerged from the deeper layers of the Sun with a certain divergence; we suppose it to proceed in the approximate direction of the structure lines of the corona (l. c. p. 597). Let its wave-length be somewhat greater than that of the absorption line; for this kind of light, the medium will then possess a positive refraction constant, and the separate rays of the beam will curve about the denser parts of the "tubular" structure. If we had supposed the wave-length to be a little less than that of the absorption line, the refraction constant would have been negative and the rays would have curved about the rarer parts of the coronal structure. In either case the divergence of our monochromatic beam will alternately diminish and increase, and this particular kind of light will reach the Earth with an intensity, determined by the degree of divergence (convergence perhaps) with which the beam left the ultimate traces of the corona.

With respect to a beam of other light, the wave-length of which differs only slightly less from that of the absorption line, the medium will have a considerably greater refraction constant, so that the rays of this particular beam may have made a bend, or part of a bend, more than those, belonging to the former beam, on their way through

¹⁾ G. E. HALE, *Astrophysical Journal*, XVI, p. 232, 1902.

²⁾ W. H. JULIUS, *Proc. Roy. Acad. Amst.* IV, p. 589—602.

the corona. This beam may, accordingly, arrive with a quite different, say a greater, divergence and consequently display a smaller intensity in the spectrum, than the neighbouring beam, first considered.

Approaching still nearer to the absorption-line we shall come across waves that reach the Earth in beams whose divergence is smaller again, showing increased intensity, etc. It is plain that in this way periodical alternations of light and dark on either side the central absorption line must arise. The waves, corresponding to the middle of one of these fringes, will have achieved exactly one whole bend (i.e. the distance between two consecutive points of inflexion of the path) more, or less, than those corresponding to the middle of the adjacent fringes.

From the familiar type of the dispersion curve it follows directly, that, in moving away from the absorption line, to equal differences in refraction constant increasing differences in wavelength will answer. The distance between the fringes will accordingly increase from the centre to either side, as has in fact been observed.

Our explanation requires besides, that this system of faint lines should be visible only when sunlight reaches us exactly along a coronal streamer of sufficient length. In my last paper (l.c.) I showed that, in case this condition is fulfilled, the average shading of the Fraunhofer lines must be abnormally weak. It is therefore not to be wondered at, that on the plate, plainly displaying the peculiar structure of H and K , the shading really was unusually faint. But the formation of a well defined line-system demands a further condition to be fulfilled, viz. that the configuration of that part of the (rotating) corona we are just looking through, offers all but the same aspect as long as the photographic plate is exposed. This, of course, requiring very special circumstances, we see why even in cases, in which the shading of the Fraunhofer lines is weak, the fringes may be missing all the same.

In a few cases has a like structure been observed with some strongly widened emission lines of the arc-spectrum. KAYSER came across this phenomenon in a line of the lead-spectrum ¹⁾; ROWLAND too seems to have observed it once; and after many vain endeavours JEWELL succeeded in obtaining a photograph of the arc spectrum of calcium, in which at H and K the series appeared rather distinctly. This plate was obtained by using an extremely powerful direct current and exposing for three or four seconds only. Under these conditions

¹⁾ H. KAYSER, Handbuch der Spectroscopie, II, p. 353.

the heated calcium vapour formed a much more extended atmosphere around the poles than with a weaker current.

KAYSER ¹⁾ asserts, though, that it has hitherto remained unknown, what are the exact conditions upon which the phenomenon depends.

In connection with the preceding considerations, I hold it possible that in those experiments the metallic vapour has, during the (short) exposures, formed a kind of flame of tubular structure, which happened to be in the exact direction of the spectroscope. This view seems reasonable if we bear in mind the well-known "blowing" which is of frequent occurrence in a powerful arc loaded with much vapour. The radiations, proceeding from the core of the arc, which caused the wide emission band, underwent anomalous dispersion in the enveloping vapour and traversed the flame-shaped streamer, following sinuous paths.

A simple experiment convinced me that the peculiar light-distribution observed in all strongly widened Fraunhofer lines ²⁾, may be strikingly imitated in the absorption-spectrum of sodium vapour. The only thing necessary was to force the absorbing vapour into a more or less tubular structure, such as we presumed it to exist in the corona.

A slightly converging beam of electric light was thrown on to the slit of a grating-spectroscope. At a distance of rather more than 100 c.m. from the slit, and about 1,5 c.m. below the axis of the beam was the opening of a specially constructed bunsen-burner, from which a sodium-flame emerged. This opening was slit-shaped (30 c.m. long, 0,2 c.m. wide) and adjusted in a position exactly parallel with the axis of the incident beam. The pressure of the gas was somewhat variable, and a good regulator unfortunately not at hand. In order to supply the long flame with sodium, the construction of the burner included a kind of narrow gutter on either side, into which had been poured a solution of a sodium-salt. This ascended into the flame by strips of asbestos paper. When viewing this flame lengthwise, it was as if one were looking through a compressed tube, the sides of which consisted of sodium-vapour. The density of the vapour diminished gradually towards the centre as well as towards the outside.

The sodium-lines were observed in the spectrum of the third order. In spite of the great length of the flame the real absorption lines were narrow; they stood out from a pretty dark softly shaded background, the width of which amounted to several ÅNGSTRÖM units. The distribution of the light entirely corresponded to JEWELL'S

¹⁾ l. c. p. 354.

²⁾ JEWELL, *Astroph. Journ.* III, p. 101; HALE, *Astroph. Journ.* III, p. 156—161.

description of the strongly shaded Fraunhofer lines. Close to the central absorption line there was also an unmistakable increase of luminosity (resembling the supposed emission lines in the solar spectrum); but this increase ought, without doubt, to be attributed to the most strongly curved rays being kept together by the tubular structure of the flame, and not to direct radiation from the flame. For, the electric light being intercepted, the emission-lines were scarcely visible in the dark field. And besides, as soon as the flame was disturbed by blowing upon it, or when it was partially covered by a diaphragm, the bright band, as well as the shading, became unsymmetrical with respect to the absorption line. Neither DOPPLER'S principle, nor the influence of pressure on wave-length can here have played an appreciable part.

I moreover observed fringe-like maxima and minima in the shadings, but they showed irregular and so unsteady, that I could not think of measuring their distances. Nor can there be any question of photographing this peculiarity before means have been devised to keep a structure of sodium vapour, as described above, steady for a reasonable time. Such means are however being prepared.

Imperfect as our present experiment must be, it still serves to bear out the assertion, that numerous peculiarities of the solar spectrum may be explained from anomalous dispersion.

Physics. — *“On the emission and absorption by metals of rays of heat of great wave-lengths.”* By H. A. LORENTZ.

§ 1. HAGEN and RUBENS have recently shown by their measurements of the reflecting power of metals ¹⁾ that the behaviour of these bodies towards rays of great wave-lengths (larger than 8μ) may be accounted for, if one applies to the propagation of electric vibrations the equations that hold for slowly varying currents, and which contain no other physical constant of the metal but its conductivity. It follows from this result that a theory which can give an adequate idea of the mechanism of a current of conduction will also suffice for the explanation of the absorption of the rays that have been used by these experimenters. A theory of this kind has been developed by RIECKE ²⁾ and DRUDE ³⁾. According to their views a metal contains an immense number of free electrons moving to and fro in much the same way as the molecules of a gas or as the ions in an electrolytic solution,

¹⁾ HAGEN and RUBENS, Berliner Sitzungsberichte, 1903, p. 269; Berichte d. deutschen phys. Gesellsch., 1903, p. 145.

²⁾ RIECKE, Wied. Ann., Bd. 66, p. 353, 1898.

³⁾ DRUDE, Drude's Ann., Bd. 1, p. 566, 1900.

the velocity of agitation increasing with the temperature. It is to be assumed that, in this "heat-motion", every electron travels along a straight line, until it strikes against a particle of the metal; the path will therefore be an irregular zigzag-line and, so long as there is no cause driving the electrons in a definite direction, an element of surface will be traversed by equal numbers of electrons, travelling to opposite sides. Things will be different if the metal is exposed to an electric force. The motion of the electrons will still be an irregular agitation; yet, motions in a definite direction will predominate, and this will show itself in our observations as an "electric current."

Now we may infer from the relation between absorption and emission that is required by KIRCHHOFF'S law, that the mechanism by which the emission of a body is produced is the same as that to which it owes its absorbing power. It is therefore natural to expect that, if we confine ourselves to the case of great wave-lengths, we shall be able to explain the emission of a metal by means of the heat-motion of its free electrons, without recurring to the hypothesis of "vibrators" of some kind, producing waves of definite periods.

In the following pages this idea has been worked out. After having calculated the emissive power we shall find that its ratio to the absorbing power does not depend on the value of those quantities by which one metal differs from another. According to the law of KIRCHHOFF, the result may be considered as representing the ratio between the emission and the absorption for an arbitrarily chosen body, or as the emissive power of a perfectly black substance; it will be found to contain a certain constant quantity, whose physical meaning will appear from the theory.

§ 2. The ratio of which I have just spoken is intimately connected with another important physical quantity, viz. the density of the energy of radiation in a space enclosed by perfectly black walls, which are kept at a uniform absolute temperature T . If the electromagnetic motions of which the aether in such a space is the seat, are decomposed into rays travelling in all directions, and each of which has a definite wave-length, the energy per unit volume, in so far as it belongs to rays with wave-lengths between λ and $\lambda + d\lambda$, may be represented by

$$F(\lambda, T) d\lambda.$$

F being a function which many physicists have tried to determine. BOLTZMANN and WIEN have shown by thermodynamical reasoning that the above expression may be written

$$\frac{1}{\lambda^5} f(\lambda T) d\lambda (1)$$

where $f(\lambda T)$ is a function of the product λT . Afterwards PLANCK¹⁾ has found for (1) the form

$$\frac{8 \pi c h}{\lambda^5} \cdot \frac{1}{e^{\frac{hc}{kT}} - 1} d\lambda (2)$$

Here c is the velocity of light in aether and h and k are universal constants.

In the theory of PLANCK every ponderable body is supposed to contain a great many electromagnetic vibrators, or, as PLANCK calls them, "resonators", each of which has its own period of free vibration, and which exchange energy with the aether as well as with the molecules or atoms of ponderable matter. The conditions of statistical equilibrium between the resonators and the aether may be thoroughly investigated by means of the equations of the electromagnetic field. As to the partition of energy between the vibrations of the resonators and the molecular motions in the body, PLANCK has not endeavoured to give an idea of the processes by which it takes place. He has used other modes of reasoning, of which I shall only mention one, which is to be found in his later papers on the subject and which consists in the determination of that distribution of energy that is to be considered as the most probable. I shall not here discuss the way in which the notion of probability is introduced in PLANCK's theory and which is not the only one that may be chosen. It will suffice to mention an assumption that is made about the quantities of energy that may be gained or lost by the resonators. These quantities are supposed to be made up of a certain number of *finite* portions, whose amount is fixed for every resonator; according to PLANCK, the energy that is stored up in a resonator cannot increase or diminish by gradual changes, but only by whole "units of energy", as we may call the portions we have just spoken of. Besides, PLANCK has found it necessary to ascribe to these units a magnitude depending on the frequency n of the free vibrations of the resonator, the magnitude being represented by $\frac{hn}{2\pi}$.

As to the constant k , it has a very simple physical meaning; $\frac{3}{2} kT$ is the mean kinetic energy of the molecule of a gas at the temperature T .

¹⁾ PLANCK, *Drude's Ann.*, Bd. 1, p. 69, 1900; Bd. 4, p.p. 553 and 564, 1901.

It appears from the above remarks that the hypothesis regarding the finite "units of energy", which has led to the introduction of the constant h , is an essential part of the theory; also that the question as to the mechanism by which the heat of a body produces electromagnetic vibrations in the aether is still left open. Nevertheless, the results of PLANCK are most remarkable. His formula represents very exactly the energy of the radiations for all values of the wave-lengths, whereas the following considerations are from the outset confined to long waves. We may at best expect to deduce from them the form which the function in (1) takes for this extreme case.

§ 3. Since, if we trust to KIRCHHOFF'S law, the ratio between the emission and the absorption must be regarded as independent of the dimensions and the position of the body considered, we may simplify the problem by an appropriate choice of circumstances. I shall therefore consider a plate with parallel plane surfaces and I shall suppose its thickness Δ to be so small that the absorption may be reckoned proportional to it and that the energy emitted by the posterior layers may be supposed to pass through the plate without any sensible absorption. I shall also confine myself to the absorption of perpendicularly incident rays and to the emission in directions making infinitely small angles with the normal.

Let σ be the conductivity of the metal, i. e. the constant ratio between the electric current and the electric force, these latter quantities being expressed in the modified electrostatic units I have lately introduced.¹⁾ Then the absorbing power of the plate, the coefficient by which we must multiply the energy of normal incident rays, in order to get the absorbed energy, is given by²⁾

$$A = \frac{\sigma}{c} \Delta \dots \dots \dots (3)$$

Here we shall substitute for σ the value furnished by DRUDE'S theory. Let the metal contain different kinds of free electrons, which we may distinguish as the 1st, the 2nd, the 3rd kind, etc., and let us suppose that all electrons of one and the same kind have equal charges, equal velocities of heat-motion, or, as we may say, "molecular" velocities, and travel over paths of equal mean length between two successive encounters with particles of the metal.

We shall write e_1, e_2, \dots for the charges of the different kinds of electrons, u_1, u_2, \dots for the mean molecular velocities, l_1, l_2, \dots

1) LORENTZ, Proceedings Acad. of Science, Amsterdam, Vol. 11, p. 608, 1903.

2) See § 12 below. In electromagnetic units the formula becomes

$$A = 4\pi c \sigma \Delta.$$

for the mean lengths of the free paths, N_1, N_2, \dots for the number of electrons of the several kinds, contained in unit of volume. We shall finally suppose, as DRUDE has done, that for every kind of electrons, the mean kinetic energy of one of these particles is equal to that of a molecule of a gas at the same temperature; we may represent it by αT , if T is the absolute temperature, and α a constant.

In these notations DRUDE'S value is ¹⁾

$$\sigma = \frac{1}{4\alpha T} (e_1^2 N_1 l_1 u_1 + e_2^2 N_2 l_2 u_2 + \dots), \quad \dots \quad (4)$$

so that (3) becomes

$$A = \frac{1}{4\alpha c T} (e_1^2 N_1 l_1 u_1 + e_2^2 N_2 l_2 u_2 + \dots) \Delta. \quad \dots \quad (5)$$

It is to be remarked that the formula (4) has been obtained in the supposition that the electric force remains constant, or at least that it keeps its direction and magnitude during an interval of time in which an electron has undergone a large number of collisions against particles of the metal. The results of HAGED and RUBENS are therefore favorable to the view that even the period of vibration of the rays is very large in comparison with the time between two succeeding impacts. Part of the following calculations are based on this assumption.

§ 4. We have now to examine the emission by the plate. It follows from the fundamental equations of the theory of electrons, that every *change*, whether in direction or in magnitude, of the velocity of an electron produces an electromagnetic disturbance travelling outwards in the surrounding aether. Hence, it will be at the instants of the collisions that the electrons become centres of radiation. We shall calculate the amount of energy, radiated in this way, in so far as it is emitted across a definite part ω of the front surface of the plate; this part of the emission is due to the electrons contained in a volume $\omega\Delta$ of the metal.

Let O be a point within the area ω , OP the normal in this point, drawn towards the side of the aether, and P a point on this line, at a distance r from O , which is very large in comparison with the dimensions of ω . In this point P we place an element of surface ω' , perpendicular to OP ; our problem will be to calculate the energy radiated across this element. I choose O as origin of coordinates and OP as the axis of z . The components of the velocity of an electron will be denoted by u_x, u_y, u_z .

¹⁾ DRUDE, l. c., p. 576. This formula does not change by the introduction of our new units.

Now, if an electron with charge e , is in O at the time t , and has at that instant the accelerations $\frac{du_x}{dt}, \frac{du_y}{dt}, \frac{du_z}{dt}$, it will produce at the point P , at the time $t + \frac{r}{c}$, a dielectric displacement, whose components are ¹⁾

$$-\frac{e}{4\pi c^2 r} \frac{du_x}{dt}, \quad -\frac{e}{4\pi c^2 r} \frac{du_y}{dt}, \quad 0 \dots \dots \dots (6)$$

On account of the great length of OP , these expressions may also be applied to an electron situated, not in O but in any other point of the part of the plate corresponding to the area ω . The whole dielectric displacement in P in the direction of x (it is only this component that will be considered in the next paragraphs) at the time $t + \frac{r}{c}$ will therefore be

$$d_x = -\frac{1}{4\pi r^2} \sum e \frac{du_x}{dt}, \quad \dots \dots \dots (7)$$

if the sum is extended to all electrons present in the volume $\omega\Delta$ at the time t .

There will also be a magnetic force of the same numerical value, and by POYNTING'S theorem a flow of energy across the element ω' , in the direction from the plate towards P . The amount of this flow per unit of time is given by

$$c d_x^2 \cdot \omega' \dots \dots \dots (8)$$

§ 5. It will be necessary for our purpose to decompose the whole emission into rays of different wave-lengths and to examine the part of (8) corresponding to the rays that have their wave-lengths within certain limits. This may be done by means of FOURIER'S series.

Let us consider a *very long* time, extending from $t = 0$ to $t = \mathfrak{D}$. During this interval the value of d_x at the point P will continually change in a very irregular way; it may however in every case be expanded in the series

$$d_x = \sum_{m=1}^{m=\infty} a_m \sin \frac{m\pi t}{\mathfrak{D}}, \quad \dots \dots \dots (9)$$

whose coefficients are given by

$$a_m = \frac{2}{\mathfrak{D}} \int_0^{\mathfrak{D}} \sin \frac{m\pi t}{\mathfrak{D}} d_x dt. \quad \dots \dots \dots (10)$$

¹⁾ The proof of this will be found in one of the next parts of my "Contributions to the theory of electrons."

Now, if the plate is kept at a constant temperature, the radiation will also be stationary and \mathfrak{d}_x^2 may be replaced by its mean value

$$\overline{\mathfrak{d}_x^2} = \frac{1}{\mathfrak{D}} \int_0^{\mathfrak{D}} \mathfrak{d}_x^2 dt$$

during the time \mathfrak{D} . Substituting the value (9), we get integrals of two different kinds, some containing the square of a sine, and others the product of two sines. The integrals of the second kind will disappear, and

$$\int_0^{\mathfrak{D}} \sin^2 \frac{m\pi t}{\mathfrak{D}} dt = \frac{1}{2} \mathfrak{D},$$

so that

$$\overline{\mathfrak{d}_x^2} = \frac{1}{2} \sum_{m=1}^{m=\infty} a_m^2. \quad \dots \dots \dots (11)$$

As to the frequency of the terms in (9), it is given by

$$n = \frac{m\pi}{\mathfrak{D}}; \quad \dots \dots \dots (12)$$

it will therefore increase by equal differences $\frac{\pi}{\mathfrak{D}}$, if we give to m its successive values.

By choosing for \mathfrak{D} a value sufficiently large, we may make this step $\frac{\pi}{\mathfrak{D}}$ as small as we like, so that ultimately, even between two values of the frequency n and $n + dn$, which are in a physical sense infinitely near each other, there will be a certain number of values of (12) and of corresponding terms in the series (11). The number of these terms will be $\frac{\mathfrak{D}}{\pi} dn$, hence, if we suppose a_m , or

$$a_m = \frac{2}{\mathfrak{D}} \int_0^{\mathfrak{D}} \sin nt \cdot \mathfrak{d}_x dt, \quad \dots \dots \dots (13)$$

to have the same value for each term of this group, the corresponding part of (11) will be

$$\frac{\mathfrak{D}}{2\pi} a_m^2 dn.$$

Substituting this for \mathfrak{d}_x^2 in (8), we get for the radiation across ω' , due to the rays with frequencies between n and $n + dn$,

$$\frac{c \mathfrak{D}}{2\pi} \omega' a_m^2 dn. \quad \dots \dots \dots (14)$$

§ 6. We have now to calculate the coefficient a_m by means of (13). After having substituted in the integral the value (7), we may still take for its limits 0 and \mathfrak{D} , provided we reckon the time from an instant, preceding by the interval $\frac{r}{c}$ the moment from which it has been reckoned till now. Thus:

$$a_m = -\frac{1}{2\pi c^2 \mathfrak{D} r} \sum \left[e \int_0^{\mathfrak{D}} \sin nt \cdot \frac{du_x}{dt} dt \right],$$

or, after integration by parts, since $\sin nt$ vanishes at the limits,

$$a_m = \frac{u}{2\pi c^2 \mathfrak{D} r} \sum \left[e \int_0^{\mathfrak{D}} \cos nt \cdot u_x dt \right]. \quad \dots \quad (15)$$

The sum in these expressions relates to all the electrons in the part $\omega\Delta$ of the plate and it is by reason of the immense number of these particles that a definite value may be assigned to a_m^2 .

We shall begin by determining a_m^2 and the amount of the radiation in the supposition that there are only free electrons of one kind (§ 3). We shall write $q = N\omega\Delta$ for their number, e for the charge of each of them, and we shall further simplify the problem by supposing that the molecular velocity u , the same for all the electrons, is not altered by the collisions and that all the paths between two successive impacts have exactly the same length l . Then, the time

$$\tau = \frac{l}{u}$$

will also have a definite length.

§ 7. Let t_1, t_2, t_3, \dots be a series of instants, between 0 and \mathfrak{D} , at intervals τ from each other. Then it is clear that, if we fix our attention on the positions of a single electron at these instants, we shall have one point on each of the sides of the zigzag-line described by this particle.

Now we may in the first place determine the integral in (15) for the lapse of time during which an electron travels over the side of the zigzag-line on which it is found at the time t_k . As the length τ of this interval is much shorter than the period $\frac{2\pi}{n}$ of the factor $\cos nt$, we may write for the integral

$$\cos nt_k \cdot \tau u_x. \quad \dots \quad (16)$$

It is clear that we shall obtain the sum in (15), for the q electrons,

if, after having multiplied (16) by e , we perform the two summations, indicated in the formula

$$a_m = \frac{u e \tau}{2 \pi e^2 \vartheta r} \sum_k [\cos n t_k \sum u_x]. \quad \dots \quad (17)$$

We have in the first place to take the sum of all the values of u_x for the system of electrons, at a particular instant t_k , and then to add together all the results obtained in this way for the instants t_1, t_2 , etc.

§ 8. If we wish to find $\sum u_x$ for a given time, we must keep in mind that the velocities u of the electrons have at that instant very different directions. We may represent all these velocities by vectors drawn from a fixed point C . The ends D of all these vectors will lie on a sphere with radius u , and if we let fall from each of these points a perpendicular DD' on the diameter of this sphere that is parallel to OX , the distances of the projections from C will give the values of u_x . The sum of all these values may therefore be represented by

$$\sum u_x = q \xi,$$

if ξ is the positive or negative distance at which the centre of gravity of the points D' , considered as equal to each other, is situated from the centre C .

Of course, on account of the large number of the points, this distance will be very much smaller than the radius u , and, if we repeat the construction of the diagram of velocities for each of the instants $t_1, t_2 \dots$, the small value that is found for ξ will be positive in one case and negative in another. It is to be remarked in this respect that there is no connexion at all between the values of ξ , which we shall find for two succeeding instants in the series $t_1, t_2 \dots$. Indeed, between any two such instants, every electron will have undergone a collision, and it may safely be assumed that, whatever be the direction of motion of an electron before the impact, all directions will be equally probable after the impact¹⁾.

Now, in order to determine a_m^2 , we have to take the square of the sum denoted by \sum in the formula (17). This square consists of terms of two kinds, some having the form

$$\cos^2 n t_k [\sum u_x]_{t_k}^2 = q^2 \cos^2 n t_k \xi_k^2 \quad \dots \quad (18)$$

¹⁾ This is easily shown, as has been done by MAXWELL in his first paper on the kinetic theory of gases, if both the electrons and the particles of the metal are supposed to be perfectly elastic spheres.

and others the form

$$2 \cos n t_k \cos n t_{k'} [\sum u_x]_{t_k} [\sum u_x]_{t_{k'}} = 2 q^2 \cos n t_k \cos n t_{k'} \xi_k \xi_{k'} \dots \quad (19)$$

As has already been said, the time \mathfrak{D} contains a very large number of periods $\frac{2\pi}{n}$. A certain value of $\cos nt$, once occurring in the series $\cos nt_1, \cos nt_2, \cos nt_3, \dots$ may therefore be supposed to repeat itself many times. Also, one and the same value of the product $\cos nt_k \cos nt_{k'}$ may be said to occur for many different values of k and k' . Such a product will therefore have to be multiplied by very different expressions of the form $\xi_k \xi_{k'}$, and, since the different values of ξ are mutually independent, the number of cases in which ξ_k and $\xi_{k'}$ have opposite signs will be equal to that in which they have the same sign. It appears in this way that the terms (19) will cancel each other in the sum. It is only the terms of the form (18) that remain, and we shall have

$$a_m^2 = \frac{n^2 e^2 \tau^2 q^2}{4 \pi^2 c^4 \mathfrak{D}^2 \gamma^2} \sum_k [\cos^2 n t_k \cdot \xi_k^2] \dots \dots \dots \quad (20)$$

§ 9. Here we may begin by taking together those terms in which $\cos nt_k$ has one and the same value. Let the number of these be Q . Then, we have to repeat Q times the construction of the diagram of velocities, and it may be asked in how many of these Q cases ξ will lie between given limits ξ and $\xi + d\xi$, or, what amounts to the same thing, what is the probability for ξ falling between these limits.

This question may be reduced to a simpler problem. A series of planes, perpendicular to OX and at equal distances from one another, will divide the spherical surface into equal parts. Therefore, instead of distributing the points D on the surface in an irregular, arbitrarily chosen manner, we may as well immediately distribute the points D' at random over the diameter, without giving any preference to one part of the line over another. The probability in question is thus found to be ¹⁾

$$Pd\xi = \frac{1}{u} \sqrt{\frac{3q}{2\pi}} e^{-\frac{3q}{2u^2} \xi^2} d\xi \dots \dots \dots \quad (21)$$

Hence, among the Q terms in the sum, occurring in (20), for which the factor $\cos^2 nt_k$ has equal values, there will be $QPd\xi$ terms, which may be said to have the same ξ_k . Together, they will contribute to the sum the amount

¹⁾ See §§ 13—15.

$$\cos^2 nt_k \cdot Q P \xi^2 d \xi$$

and the total sum of all the Q terms is got from this by an integration which we may extend from $\xi = -\infty$ to $\xi = +\infty$. Consequently, the sum of those Q terms will not be altered, if, in each of them, we replace ξ^2_k by

$$\overline{\xi^2} = \int_{-\infty}^{+\infty} P \xi^2 d \xi \dots \dots \dots (22)$$

This expression being the same whatever be the particular value of $\cos^2 nt_k$, the sum in (20) at once becomes

$$\overline{\xi^2} \sum_k [\cos^2 nt_k]. \dots \dots \dots (23)$$

Again, since the instants t_1, t_2, \dots are uniformly distributed at distances that are very small parts of the period $\frac{2\pi}{n}$, the sum will remain the same, if in every term we write $\frac{1}{2}$ instead of $\cos^2 nt_k$. The number of terms being $\frac{\vartheta}{\tau}$, we find for (23)

$$\frac{\vartheta}{2\tau} \overline{\xi^2}$$

and for (20)

$$a^2_m = \frac{n^2 e^2 \tau q^2}{8\pi^2 c^4 \vartheta r^2} \overline{\xi^2}.$$

We have by (21) and (22)

$$\overline{\xi^2} = \frac{n^2}{3q};$$

hence, replacing τ by $\frac{l}{n}$, we find

$$a^2_m = \frac{n^2 e^2 q l u}{24\pi^2 c^4 \vartheta r^2} = \frac{n^2 e^2 N l u \Delta}{24\pi^2 c^4 \vartheta r^2} \omega$$

and for the emission (14), in so far as it is due to the one kind of electrons that has been considered

$$\frac{n^2 e^2 N l u \Delta}{48\pi^3 c^3 r^2} \omega \omega' d n.$$

This value must still be multiplied by 2 because we may apply to the second of the components (6) the same reasoning as to the first component, and the total radiation from the plate may obviously be considered as the sum of all the values corresponding to the

different kinds of electrons. The final result is therefore¹⁾

$$\frac{n^3}{24\pi^3 c^3 \tau^2} (e_1^2 N_1 l_1 u_1 + e_2^2 N_2 l_2 u_2 + \dots) \Delta \omega \omega' dn. \quad (24)$$

§ 10. If now we divide (24) by (5), all quantities N, e, u and l , by which one metal differs from another, disappear. This is what might be expected according to KIRCHHOFF'S law and the result

$$\frac{an^2 T}{6\pi^3 c^2 \tau^3} \omega \omega' dn$$

may be taken to express the emission by a perfectly black body under the circumstances we have supposed. It represents the amount of energy which, in the case of such a body, is transmitted per unit of time across an element ω' , in the rays whose frequency lies between n and $n + dn$ and whose directions deviate infinitely little from the normal to the element, being contained within a solid angle $\frac{\omega}{r^2}$. Multiplying by $\frac{4\pi r^2}{c\omega\omega'}$, we are led to the following expression for the density of energy of which I have spoken in § 2 :

$$\frac{2an^2 T}{3\pi^2 c^3} dn. \quad (25)$$

Taking for the group of rays those whose wave-lengths are included between λ and $\lambda + d\lambda$, we get for the corresponding energy per unit volume

$$\frac{16 \pi a T}{3 \lambda^4} d\lambda. \quad (26)$$

¹⁾ It is easy to free ourselves from the hypothesis that for all electrons of one kind there is a single length of path l and a single molecular velocity u . Indeed, the motion of an electron along one of the small straight lines l , which it describes between the instants 0 and \mathcal{S} , will furnish for the sum in (15) a quantity

$$e \cos nt \cdot u_x \tau,$$

if u is the velocity for the particular line l we wish to consider, and τ the time required for the motion along it.

Now, among all these rectilinear motions between two successive encounters, of one kind of electrons, we may select those for which u and l have certain definite values and we may begin by calculating the coefficient a_m and the emission, in so far as they depend on the part of (15) which corresponds to these particular motions; in doing so, we may use the method shown in §§ 7—9. The total emission may be regarded as the sum of all the partial values (with different l 's and different u 's) thus obtained, and after all the expression (24) will still hold, provided we understand by $l_1, l_2 \dots$ certain mean lengths of path and by $u_1, u_2 \dots$ certain mean molecular velocities. We need not however enter into these details, because the conductivity and the coefficient of absorption have not been calculated with a corresponding degree of accuracy.

This is found from (25) by using the relation $n = \frac{2\pi c}{\lambda}$.

§ 11. The result of the preceding calculations not only conforms to the law of KIRCHHOFF; it has also a form agreeing with those of BOLTZMANN and WIEN. Indeed, the expression (26) follows from (1), if we put

$$f(\lambda T) = \frac{16}{3} \pi a \cdot \lambda T.$$

Our last task will be to evaluate the constant a by applying the formula (26) to experimental determinations of the radiation of black bodies, and to compare the result with what has been inferred about the same constant from other classes of phenomena. Combining the measurements of LUMMER and PRINGSHEIM¹⁾, who have gone far into the infra-red, with the absolute amount of the radiation as determined by KURLBAUM²⁾, I find

$$a = 1,6 \cdot 10^{-16} \frac{\text{erg}}{\text{degree}}.$$

On the other hand, we get, starting from VAN DER WAALS' evaluation of the mass of an atom of hydrogen,

$$a = 1,2 \cdot 10^{-16}.$$

A comparison of my formula with that of PLANCK is also interesting. For very large values of the product λT , the denominator in (2) becomes $\frac{ch}{k\lambda T}$, and the expression itself $\frac{8\pi kT}{\lambda^4} d\lambda$. This agrees with (26), if $a = \frac{3}{2} k$.

Now the mean kinetic energy of a molecule of a gas would be $\frac{3}{2} kT$ according to PLANCK and has been represented in what precedes by aT . There appears therefore to be a full agreement between the two theories in the case of long waves, certainly a remarkable conclusion, as the fundamental assumptions are widely different.

On the absorption by a thin metallic plate.

§ 12. Take the origin of coordinates in the front surface, the axis of z towards the metal, and let there be free aether on both sides.

Writing \mathfrak{E} for the electric force, \mathfrak{J} for the current of conduction,

¹⁾ LUMMER and PRINGSHEIM, Verhandl. d. deutschen phys. Gesellsch., 1900, p. 163.

²⁾ KURLBAUM, Wied. Ann., Bd. 65, p. 754, 1898.

\mathfrak{H} for the magnetic force and putting the magnetic permeability = 1, we have for the metal

$$\text{rot } \mathfrak{H} = \frac{1}{c} \mathfrak{J}, \quad \text{rot } \mathfrak{E} = -\frac{1}{c} \dot{\mathfrak{H}}, \quad \mathfrak{J} = \sigma \mathfrak{E}.$$

It is found by these equations that in electromagnetic waves travelling in the direction of the positive z , \mathfrak{E} and \mathfrak{H} can have the directions of OX and OY , and values equal to the real parts of the complex quantities

$$\mathfrak{E}_x = a e^{int - \kappa(1+i)z}, \quad \mathfrak{H}_y = \kappa a e^{int - \kappa(1+i)z} \quad \dots \quad (27)$$

a being the amplitude of the electric force, and the constants α and κ being given by

$$\alpha = \frac{1}{c} \sqrt{\frac{1}{2} n \sigma}, \quad \kappa = (1-i) \sqrt{\frac{\sigma}{2n}}.$$

Similarly, waves travelling in the opposite direction may be represented by

$$\mathfrak{E}_x = a e^{int + \kappa(1+i)z}, \quad \mathfrak{H}_y = -\kappa a e^{int + \kappa(1+i)z} \quad \dots \quad (28)$$

For the aether the corresponding formulae are somewhat simpler; in the first case

$$\mathfrak{E}_x = a e^{int - i \frac{n}{c} z}, \quad \mathfrak{H}_y = a e^{int - i \frac{n}{c} z} \quad \dots \quad (29)$$

and in the second

$$\mathfrak{E}_x = a e^{int + i \frac{n}{c} z}, \quad \mathfrak{H}_y = -a e^{int + i \frac{n}{c} z} \quad \dots \quad (30)$$

Now, if rays fall perpendicularly on the front surface of the plate, we may unite all the systems of waves arising from the repeated reflexions into the following parts: 1st. a reflected system in the aether, 2nd. transmitted waves in the aether behind the plate, 3rd. waves in the plate, travelling towards the back surface and 4th. rays in the metal, going in the opposite direction. Representing the incident rays and the motions mentioned under these four heads by the equations (29), (30), (29), (27), (28), with the values a_1, a_2, a_3, a_4, a_5 of the amplitude, we have, in virtue of the conditions at the two surfaces (continuity of \mathfrak{E}_x and \mathfrak{H}_y)

$$\begin{aligned} a_1 + a_2 &= a_4 + a_5, \\ a_1 - a_2 &= \kappa(a_4 - a_5), \\ a_4 e^{-s} + a_5 e^{+s} &= a_3 e^{-i \frac{n}{c} \Delta}, \\ \kappa a_4 e^{-s} - \kappa a_5 e^{+s} &= a_3 e^{-i \frac{n}{c} \Delta}. \end{aligned}$$

In these formulae, Δ is the thickness of the plate, and

$$\alpha(1+i)\Delta = s \quad \dots \quad (31)$$

The solution, in so far as it is necessary to our purpose, is

$$a_2 = \frac{(\alpha^2 - 1)(e^{-s} - e^{+s})}{(\alpha + 1)^2 e^{+s} - (\alpha - 1)^2 e^{-s}} a_1,$$

$$a_3 = \frac{4\alpha}{(\alpha + 1)^2 e^{+s} - (\alpha - 1)^2 e^{-s}} e^{i\frac{\pi}{c}\Delta} a_1.$$

In these expressions Δ and consequently s are now to be supposed infinitely small. Replacing e^{-s} and e^{+s} by $1-s$ and $1+s$, one finds

$$a_2 = -\frac{1}{2}\left(\alpha - \frac{1}{\alpha}\right)s a_1,$$

$$a_3 = \left[1 - \frac{1}{2}\left(\alpha + \frac{1}{\alpha}\right)s\right] e^{i\frac{\pi}{c}\Delta} a_1$$

The first of these equations shows that the amplitude of the rays reflected by the thin plate is infinitely small, so that we may neglect their energy as a quantity of the second order.

As to the transmitted rays, the amount of energy propagated in them will be equal to the product of the incident energy by the square of the modulus of the complex expression

$$\left[1 - \frac{1}{2}\left(\alpha + \frac{1}{\alpha}\right)s\right].$$

This square is

$$1 - \frac{\sigma}{c}\Delta,$$

whence we deduce for the coefficient of absorption

$$A = \frac{\sigma}{c}\Delta.$$

On the probability with which one may expect that the centre of gravity of a large number of points distributed at random on a limited straight line will lie within given limits.

§ 13. Divide the line into a large number p of equal parts, and call these, beginning at the end A of the line, the 1st, the 2nd, the 3rd part, etc. Denote by q the number of points and let q be very much larger than p .

We shall imagine the points to be placed on the line one after another, in such a way that, whatever be the position of the points already distributed, a new point may as well fall on one part of

the line as on the other. The result will be a certain distribution of the whole number, entirely determined by chance. Let us conceive this operation to be very often repeated, say Q times, and let us calculate in how many of these Q cases, a desired distribution of the points over the p parts will occur. Dividing by Q we shall have the probability of the distribution.

The probability that there will be $a, b, \dots m$ points on the 1st, 2nd, p th part of the line ($a + b + \dots + m = q$), is given by

$$P = \left(\frac{1}{p}\right)^q \frac{q!}{a! b! \dots m!}.$$

In the case of a very large value $\frac{q}{p}$, this probability becomes extremely small, as soon as one of the numbers $a, b, \dots m$ is far below $\frac{q}{p}$. Neglecting these small probabilities, we shall confine ourselves to those cases, in which each of the numbers $a, b, \dots m$ is very large. Then, by the well known formula of STIRLING,

$$a! = \sqrt{2a\pi} \left(\frac{a}{e}\right)^a, \text{ etc.}$$

and, if we put

$$\frac{a}{q} = a', \frac{b}{q} = b', \dots \frac{m}{q} = m',$$

we shall find

$$\log P = -\frac{1}{2}(p-1) \log(2\pi q) - q \log p - [(a'q + \frac{1}{2}) \log a' + \dots + (m'q + \frac{1}{2}) \log m'] \quad (32)$$

It is to be remarked that the numbers $a, b, \dots m$ can only increase or diminish by whole units. The numbers $a', b' \dots m'$ can change by steps equal to $\frac{1}{q}$; this may be made so small that they may be considered as continuously variable.

§ 14. We shall in the first place determine the values of $a', b', \dots m'$ for which the probability P becomes a maximum. We have

$$d \log P = - \left[\left(q + \frac{1}{2a'} + q \log a' \right) da' + \dots + \left(q + \frac{1}{2m'} + q \log m' \right) dm' \right],$$

with the condition

$$da' + \dots + dm' = 0,$$

which is a consequence of

$$a' + \dots + m' = 1 \quad (33)$$

The maximum will therefore be reached if

$$a' = b' = \dots = m' = \frac{1}{p},$$

so that the uniform distribution will be the most probable.

We shall next consider the probability for a distribution differing a little from the most probable one. Let us put

$$a' = \frac{1}{p} + \alpha, \quad b' = \frac{1}{p} + \beta, \quad \dots, \quad m' = \frac{1}{p} + \mu. \quad (34)$$

and let us suppose the numbers $\alpha, \beta, \dots, \mu$, to be so small in comparison with $\frac{1}{p}$, that in the expansion of the quantities in (32) in ascending powers of $\alpha, \beta, \dots, \mu$, we may neglect all powers surpassing the second. We have for instance

$$\left(a'q + \frac{1}{2}\right) \log a' = -\left(\frac{q}{p} + \frac{1}{2}\right) \log p + \left(q + \frac{1}{2}p - q \log p\right)\alpha + \frac{1}{2}p\left(q - \frac{1}{2}p\right)\alpha^2,$$

where, in the last term, we may omit the term $\frac{1}{2}p$, because it is much smaller than q . If we put

$$-\frac{1}{2}(p-1) \log(2\pi q) + \frac{1}{2}p \log p = \log P_m$$

and keep in mind that, in virtue of (33),

$$\alpha + \beta + \dots + \mu = 0, \quad \dots \quad (35)$$

the equation (32) becomes

$$\log P = \log P_m - \frac{1}{2}p q (\alpha^2 + \beta^2 + \dots + \mu^2),$$

$$P = P_m e^{-\frac{1}{2}p q (\alpha^2 + \beta^2 + \dots + \mu^2)}.$$

It is seen from this that P_m is the maximum of the probability, with which we shall have to do, if $\alpha = \beta = \dots = \mu = 0$. The equation shows also that, conformly to what has been said above, the probability will only be comparable to P_m so long as $\alpha, \beta, \dots, \mu$ are far below $\frac{1}{p}$. Indeed, if one of these numbers had this last value, P_m would be multiplied by

$$e^{-\frac{q}{2p}},$$

which, by our assumptions, is extremely small.

§ 15. Let $2u$ be the length of the line, x the distance along the line, reckoned from the end A , and let us take $\frac{u}{p}$ for the value or

this coordinate for all points situated on the first part of the line, $3 \frac{u}{p}$ for all points of the second part, and so on. Then, in the distribution that is characterized by $a', b', \dots m'$, the coordinate of the centre of gravity of the q points will be

$$[a' + 3 b' + 5 c' + \dots + (2 p - 1) m'] \frac{u}{p}.$$

or, by (34),

$$u + [a + 3 \beta + 5 \gamma + \dots + (2 p - 1) \mu] \frac{u}{p}.$$

The positive or negative value of

$$\xi = [a + 3 \beta + 5 \gamma + \dots + (2 p - 1) \mu] \frac{u}{p} \dots (36)$$

is thus seen to represent the distance between the middle point of the line and the centre of gravity. We have to calculate the probability for this distance lying between ξ and $\xi + d\xi$.

The problem is easily solved by means of a change of variables. Instead of the quantities $a, \beta, \dots \mu$, which serve to define a mode of distribution, we shall introduce new ones $a', \beta', \dots \mu'$, the substitution being linear and orthogonal.

Let us take for the first of the new variables

$$a' = \frac{1}{\sqrt{p}} a + \frac{1}{\sqrt{p}} \beta + \dots + \frac{1}{\sqrt{p}} \mu, \dots (37)$$

and for the second

$$\beta' = -\frac{p-1}{z} a - \frac{p-3}{z} \beta - \dots + \frac{p-1}{z} \mu, \dots (38)$$

where the numerators form an arithmetical progression, whereas z means the positive square root of the sum of the squares of the numerators. These expressions (37) and (38) may really be adopted, because the peculiar conditions for an orthogonal substitution are satisfied: in both expressions the sum of the squares of the coefficients is 1, and we get 0 if we add together the coefficients of (37) after having multiplied them by the corresponding coefficients in (38). As to the coefficients in the expressions for $\gamma', \dots \mu'$, we may choose them as we like, provided the whole substitution remain orthogonal.

The reason for the above choice of a' and β' will be clear; the condition (35) simplifies to

$$a' = 0 \dots (39)$$

and, in virtue of (35), the value (36) will be equal to

$$\xi = \frac{z u}{p} \beta' \dots (40)$$

in all cases with which we are concerned.

Now, the modes of distribution for which the value of ξ lies between ξ and $\xi + d\xi$ are those for which β' lies between β' and $\beta' + d\beta'$, if

$$d\beta' = \frac{p}{\alpha u} d\xi. \dots \dots \dots (41)$$

Since $\alpha' = 0$, every mode of distribution may be defined by the values of $\beta' \dots \mu'$, these quantities being, like $\alpha, \beta, \dots \mu$, capable of very small variations.

We can therefore select, among all the modes of distribution, those for which $\beta' \dots \mu'$ lie between β' and $\beta' + d\beta'$, γ' and $\gamma' + d\gamma'$, etc. The number of these may be represented by

$$h d\beta' \dots d\mu', \dots \dots \dots (42)$$

where h is a coefficient whose value need not be specified. It suffices to know that it is independent of the values chosen for $\beta' \dots \mu'$. This is a consequence of the linear form of the relations between these variables and $a, b, \dots m$.

As the just mentioned modes of distribution, whose number is given by (42), differ infinitely little from one another, the probability P may be taken to be the same for each of them. Hence, the probability for the occurrence of one of these modes, no matter which, must be

$$h P d\beta' \dots d\mu' \dots \dots \dots (43)$$

From this we may pass to the probability for β' lying between β' and $\beta' + d\beta'$, whatever be the values of $\gamma' \dots \mu'$; we have only to integrate with respect to these last variables. Now using the fundamental property of an orthogonal substitution

$$\alpha^2 + \beta^2 + \dots + \mu^2 = \alpha'^2 + \beta'^2 + \dots + \mu'^2,$$

and attending to (39), we write for (43)

$$h P_m e^{-\frac{1}{2} p q (\beta'^2 + \dots + \mu'^2)} d\beta' \dots d\mu'.$$

If we integrate this expression from $-\infty$ to $+\infty$, as may be done for obvious reasons, denoting by k a coefficient that does not depend on β' , we find for the probability in question

$$k e^{-\frac{1}{2} p q \beta'^2} d\beta'.$$

On account of (40) and (41) this is equal to

$$k' e^{-\frac{p^3 q}{2\alpha^2 u^2} \xi^2} d\xi. \dots \dots \dots (44)$$

k' being a new constant.

It remains to introduce the value of x^2 . According to the definition of this quantity, it is $\frac{1}{3} p(p^2-1)$, instead of which we may take $\frac{1}{3} p^3$, because p is a very large number. In this way (44) changes into

$$k' e^{-\frac{3q}{2a^2} \xi^2} d\xi. \dots \dots \dots (45)$$

We may finally determine the coefficient k' by remarking that (45), integrated from $-\infty$ to $+\infty$, must necessarily give 1. This requires that

$$k' = \frac{1}{u} \sqrt{\frac{3q}{2\pi}},$$

so that our result becomes

$$\frac{1}{u} \sqrt{\frac{3q}{2\pi}} e^{-\frac{3q}{2a^2} \xi^2} d\xi.$$

Microbiology. — “*The decomposition of cellulose by aërobic micro-organisms.*” By G. VAN ITERSON JR. (Communicated by Prof. M. W. BEIJERINCK).

(Communicated at the meeting March 28, 1903).

When we introduce into the soil or into natural waters substances consisting of cellulose, such as linen, cotton or paper, it will be seen, that the greater part comparatively soon disappears, whilst the cellulose derived from the continually falling dead leaves and other parts of plants is also soon destroyed under natural conditions either totally or partly. It is also a known fact that the layer of humus in the primeval forests has a limited thickness, the decrease being just compensated by the increase caused by the falling of the leaves. Investigation shows that the cellulose, although chemically so stable, is decomposed by micro-organisms. The observations by MITSCHERLICH ¹⁾, POPOFF ²⁾, VAN TIEGHEM ³⁾, TAPPEINER ⁴⁾, VAN

¹⁾ Ueber die Zusammensetzung der Wand der Pflanzenzelle, Monatsber. d. Berl. Akad., 1850, p. 102.

²⁾ Ueber Sumpfgasgähmung, Archiv. f. ges. Physiol., 1875, Bd. 10, S. 113.

³⁾ Sur le bacillus amylobacter et son rôle dans la putréfaction des tissus végétaux, C. R. t. 88, 1879, p. 88. — Identité du bacillus amylobacter et du vibron butyrique de M. Pasteur, C. R. t. 89, 1879, p. 5.

⁴⁾ Ueber Celluloseverdauung, Ber. d. d. ch. G. Bd. 15, 1882, S. 999. — Ueber Cellulosegähungen, Ber. d. d. ch. G. Bd. 16, 1883, S. 1734. — Ueber die Sumpfgasgähmung im Schlamm der Teiche, Sümpfe u. Kloaken, Ber. d. d. ch. G. Bd. 16, 1883, S. 1740.

SEXUS¹⁾ and particularly those of HOPPE SEYLER²⁾ and of OMELIANSKI³⁾ proved, that cellulose may be broken up by anaërobic bacteria, with production of methane and carbon dioxide, or hydrogen and carbon dioxide and simultaneous formation of acetic and butyric acids. In this communication it will be shown that cellulose may also be rendered soluble by aërobic bacteria. In the first place it was proved, that this substance may serve as a source of carbon for denitrifying bacteria and may, therefore, be made to disappear with great rapidity in the presence of nitrates. But it could also be shown that cellulose is fit as a carbonfood for common aërobic bacteria and although the solution then takes place slowly, there can be no doubt about the decomposition. The products derived from the cellulose play an important role in the nutrition of other microbes particularly the spirillae, so that an elegant accumulation experiment may be based on the use of cellulose as a source of carbon.

Although the destruction of cellulose by anaërobic or aërobic bacteria requires a faintly alkaline medium, it may, with sufficient aëration, also be acted on in a faintly acid surrounding by various moulds and mycelia of higher fungi. This was first demonstrated in 1886 by DE BARY for the genus *Peziza* and the same was shown by later observers for other moulds, whilst the destruction always appeared to be due to the action of an enzyme. Here we will prove that the power possessed by moulds to attack cellulose is not confined to certain species only, as one might imagine from the existing literature, but that a great number of the species of this group share that property.

Finally, I wish to observe that I will occupy myself exclusively with the destruction of *pure* cellulose and not with that of lignified and corky cell-walls, where in the first place higher fungi are at work, as is shown by the researches of R. HARTIG⁴⁾.

1. *The decomposition of cellulose by denitrifying bacteria.*

MEUSEL⁵⁾ states in 1871 that in the presence of cellulose bacteria

¹⁾ Bijdrage tot de kennis der cellulosegisting. Dissertation, Leonards, at Leiden, 1890, (this contains a very complete literary review).

²⁾ Ueber die Gährung der Cellulose mit Bildung von Methan u. Kohlensäure, Zeitschr. f. Phys. Ch. Bd. 10, 1886, S. 401.

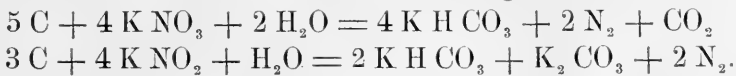
³⁾ Sur la fermentation de la cellulose, C. R. t. 121, 1895, p. 653. — Sur un ferment de la cellulose, C. R. t. 125, 1897, p. 970. — Sur la fermentation cellulosique, C. R. t. 125, 1897, p. 1131. — Ueber die Gährung der Cellulose, Centrbl. f. Bakt. Abt. II, Bd. 8, 1902, S. 193.

⁴⁾ Die Zersetzungserscheinungen des Holzes, Berlin 1878.

⁵⁾ De la putréfaction produite par les bactéries en présence des nitrates alcalins C. R. t. 81, 1876, p. 533. Nitritbildung durch Bacterien, Ber. d. d. ch. G. Bd. 8, 1875, S. 1214.

reduce nitrates to nitrites; he has, therefore, proved denitrification, in the largest sense of the word, as being possible with cellulose, but from his short notes we do not understand his *modus operandi* or the nature of the cellulose used in the experiments. DEHÉRAIN¹⁾ positively states in 1897 that he has not been able to observe denitrification with flax fibres and the attention of OMELIANSKI (l.c.) has also not been attracted to this process when engaged in the study of the fermentations of cellulose. This investigator induces the methane or hydrogen fermentation by means of a nitrogenous food composed of ammonium sulphate or phosphate and sometimes he also adds asparagine, peptone, extract of meat or of manure. Strange to say, he has not worked with nitrates; had he done so, he would have noticed that the nature of the process is completely modified, for instead of the methane or hydrogen fermentation denitrification sets in which is characterised by the production of free nitrogen and carbon dioxide.

In a previous research²⁾ on accumulation experiments with denitrifying bacteria, I have shown that these aërobic organisms can oxidise many different organic substances out of contact with air with the aid of nitrates or nitrites, according to the formulæ:



Denitrification was noticed with lactates, tartrates, citrates, malates, acetates, glucose, starch, asparagine, gelatin, broth, methyl and ethyl alcohol and it was, therefore, thought worth while to try whether cellulose might also be used as a source of carbon supply in the denitrification process, which indeed proved to be the case.

Before describing my experiments in detail, I will first make some remarks as to the nature of the cellulose employed. As a rule Swedish filterpaper was taken. Although this paper gives a faint blue colour with a dilute solution of iodine it was found to be very difficult to remove the impurity with boiling water; the so-called starch-free paper from SCHLEICHER and SCHÜLL, which has been purified with hydrofluoric acid, showed the same reaction. Sometimes linen tissues and cottonwool were used, from which the first also gives a blue coloration with dilute solutions of iodine, whilst the latter does not show this reaction. The little impurities, present in the cellulose employed, were however, of no moment in my experiments, as the effect on the cell walls was judged by the changes observed by a microscopical investigation.

¹⁾ Recherches sur la réduction des nitrates, Ann. agron. t. 23, 1897.

²⁾ VAN ITERSOM, Accumulation experiments with denitrifying bacteria. Proc. Acad. of Science, Amsterdam July 1902.

I obtained the best results with a paper pulp prepared by triturating Swedish filterpaper in water, care being taken that this pulp contained 2% of cellulose.

In order to obtain a thorough denitrification with cellulose, a bottle holding about 200 cc. is filled with the following mixture:

Tapwater ¹⁾ 100, paper 2, KNO₃ 0,25, K₂HPO₄ 0,05,

and the mixture is then inoculated with a few cc. of mud (from a ditch).

The bottle is then quite filled up in the manner described in my former communication (l.c.), to prevent access of air, and the cultivation takes place at 35°.

After the lapse of about 8 days the action is perceptible, but only after 12 days a brisk fermentation sets in. The cellulose is carried to the top by the generated gasbubbles and a quantity of liquid is forced out of the bottle by the slimy froth, while the paper-pulp is kept back by the stopper. In the beginning of the process a strong formation of nitrite may be observed, but the nitrates and nitrites soon decrease and after the lapse of about 15 days, these compounds have disappeared. The liquid is now carefully decanted from the pulp, which may be done without appreciable loss of paper fibres, as these readily agglomerate. The bottle is then refilled with the following liquid:

Tapwater 100, KNO₃ 0,25, K₂HPO₄ 0,05.

The process now starts much quicker than in the first cultivation, the nitrate disappears in 4 or 5 days and by repeating the operation a few times more, cultures may be obtained of an increasingly active denitrifying power, with which it is possible to completely reduce in one or two days 0.5 gram of KNO₃ dissolved in 200 cc. of water. This method of working is preferable to adding a fresh quantity of KNO₃ to the original culture, as it is then not possible to reduce on the whole more than about 1/2 % of KNO₃ (calculated in regard to the quantity of the liquid used, or 25 % in regard to the cellulose) because the process then comes to a standstill by the alkaline potassium carbonate formed from the nitrate.

If now a sterilised liquid is inoculated with the strongly denitrifying rough culture and the cultivation allowed to take place under the same circumstances as described above, the action commences much more rapidly than in the first preliminary experiment, whilst the same phenomena occur. Even after repeating the inoculation ten times, no change in the intensity of the process could be observed.

Not only paper, but raw flax fibres, cottonwool and linen appeared

¹⁾ From the Downs at Loosduinen.

capable of inducing denitrification, the cottonwool, however, being attacked with great difficulty. No denitrification could be observed with sawdust or turf, whilst VAN SENUS (l. c. pg. 104) has also been unable to observe decomposition of wood-cellulose by real anaerobic bacteria. This extraordinary difficult decomposition of wood-cellulose out of contact with the air, is, according to this investigator, perhaps the key to the explanation of the formation of humine substances, peat, brownecoal and coal.

The distribution of the microbes, engaged in the denitrification of cellulose, in the mud from canals, seems to be a very general one, as each sample employed contained these germs. Although they are also very generally distributed in the earth, their number per cc. appears therein to be less, for, on using earth as infecting material, the action was delayed. Even in sea water, taken from the port of den Helder, were always microbes found, which in the presence of cellulose could induce denitrification; in how far these forms are similar to the terrestrial ones has not yet been ascertained, but I wish to call particular attention to the fact, that, at least near the shore, cellulose may disappear by denitrification.

The changes, which cellulose undergoes during this process, are visible to some extent with the naked eye: the white fibres soon turn orange and the pulp acquires a viscous consistency. Microscopically, it appears, that already very soon after inoculation some of the fibres are inclosed in a bacterial mucus and after a prolonged culture this is the case with nearly all the fibres. At first, the whole of the fibre is still very plainly visible within this mucus, but gradually, on account of the decomposition, it completely disintegrates into loose fibrillae and at last we only find a few particles of cellulose left, or the fibre disappears altogether (fig. 1). This destruction of the cellulose becomes very pronounced, when instead of paper-pulp strips of filterpaper are used. By repeatedly adding fresh nitrate we then finally obtain bacteria-membranes, which still have the exact shape of the strips of paper but in which we only meet isolated fibres disintegrated into fibrillae or even still more decomposed. As is already stated, the woody substance is not attacked by denitrifying bacteria, the few annulated, spiral and pitted vessels, which are contained as impurities in the filterpaper, are found unaltered in this mucus. Fig. 2 shows the form of two very strongly dissolved paperfibres (*a*) and some non-attacked woody elements (*β*, *γ* and *δ*), which are still found in such preparations.

The gases, liberated during the denitrification of cellulose and of

which some litres were collected, consist exclusively of free nitrogen and carbon dioxide; no trace of hydrogen, methane or nitrous oxide (N_2O) was found.

As regards the micro-organisms which take part in this process, a microscopical examination of the said bacterial mucus, which consists of a finely granulated substance, shows the presence of very small rod-like bacteria (fig. 1) and further there are found in the cultures infusoria, amœbae, monads, spirillae, other small bacteria and vibriœnae; larger rod-bacteria or spore-forming organisms were not detected. That the bacteria, involved in the process, are no spore forming organisms, was also shown by the fact, that no pasteurised material of whatever origin (mud from a ditch or from the soil) can cause denitrification in the presence of cellulose.

Many experiments have been made with the object of isolating the bacteria taking part in the denitrification, but always with a negative result. By inoculation on meat-gelatin and cultivating at 24° , I several times obtained pure cultures of *Bacillus stutzeri* NEUM. and LEHM., which bacterium was also found in large numbers in those cases where other denitrifying bacteria were present, so that denitrification with cellulose is a new accumulation experiment for this important species, which, however, does not attack the cellulose itself.

On using meat-agar or one of the following culture liquids:

Tapwater 100, agar 2, sodium lactate 2, KNO_3 0,05, K_2HPO_4 0,05,
Tapwater 100, agar 2, glucose 2, KNO_3 0,05, K_2HPO_4 0,05,

and cultivating at 35° , other bacteria besides *B. stutzeri* were found and these were nearly always denitrifying ones. Very often a mucous colony of a motionless, non-spore forming denitrifying bacterium became conspicuous, while in other cases a small, slightly denitrifying spirillum may be isolated. No permanent denitrification with paper could, however, be obtained with any of these forms or with any combination thereof, even the crude mixture as it is formed on the plates was not capable to do this. The fact, that these bacteria may cause a temporary faint evolution of gas (which, at first, made me suspect, that the destruction of cellulose could be accomplished by ordinary denitrifying bacteria) must be attributed to the presence of small quantities of impurities in the cellulose. Still, I think we may take it for granted, that we are dealing here not with an anaërobic but with an aërobic bacterium, first of all, because all known denitrifying bacteria are aërobic and only behave anaërobically in the presence of saltpetre, secondly because methylene-blue is not reduced; when added to a medium in which cellulose is denitrifying, whilst in

cultures of the known anaërobie bacteria this compound is always decolorised. We therefore come to the conclusion, that the bacterium, which causes the denitrification of cellulose, does not grow on the used nutrient media, or else, growing there, loses immediately its denitrifying properties.

If now we compare the hydrogen and methane fermentations with the denitrifying process we find the following points of difference.

1st. In the hydrogen or methane fermentation the liberated gaseous products are carbon dioxide and hydrogen, or carbon dioxide and methane.

2nd. To those fermentations chalk must be added to neutralise the formed butyric and acetic acids, whilst in our case the saltpetre yields potassium carbonate and no volatile acids can be detected.

3rd. Those processes take place in a medium wherein sulphates can be reduced to H_2S and therefore methylene-blue is decolorised. In my experiments such a reduction of sulphates is quite out of the question as long as traces of nitrates and nitrites are still present.

4th. The methane and hydrogen fermentation are caused by comparatively large, well characterised spore forming organisms, our denitrification by very small bacteria, forming no spores.

The velocity with which cellulose disappears during the denitrification is about the same as in the methane or hydrogen fermentation of this substance. In a volume of 500 c.c., I succeeded in completely dissolving 8 grams of cellulose all but a few fibres, by means of 36 grams of KNO_3 , in a month's time. The quantity of KNO_3 theoretically required amounts to only 24 grams, but in my experiments a portion of the nitrate was lost in the expelled liquid and, therefore, more nitrate was required. By means of the hydrogen fermentation, OMELANSKI succeeded in dissolving 41.6 grams of cellulose contained in a volume of 3 litres in $3\frac{1}{2}$ months, and about 12 grams in a volume of 1 litre in 5 months, which velocities agree with the values found by me for the denitrification.

Notwithstanding the possibility of denitrification of saltpetre under the influence of cellulose, in the presence of this substance nitrification of ammonium salts and nitrites can proceed without interruption. This has already been shown by OMELANSKI¹⁾, who cultivated the nitrite ferment on paper. We also observed nitrification of ammonium salts and nitrites, when a very small quantity of cellulose (about

¹⁾ Kleinere Mitteilungen über Nitrifikationsmikroben I, Centrbl. f. Bakt. Abt. II, Bd. 8, 1902, S. 785.

0,05 %) was introduced into a thin layer of one of the following culture liquids, which were inoculated with earth:

Tapwater 100, NH_4Cl 0,05, K_2HPO_4 0,05,
 or " " KNO_2 0,05, " 0,05,

In my previous communication I have already pointed out, that nitrification and denitrification may take place together in garden soil and that the aëration decides, which of these processes will be the predominant one; the same conclusion may, therefore, now be drawn for cellulose as a nutrient material. A closer examination however shows, that the two processes cannot occur simultaneously in the same particle, but that a localisation must take place, in this way, that strong aëration is necessary in the particles where nitrification sets in, whilst the exclusion of air is necessary for the denitrification process.

As has already been previously observed formation of nitrite takes place in the first stage of the denitrification process in the presence of cellulose and as this substance by no means prevents the oxidation of the nitrite to nitrate, these two processes, occurring simultaneously, may cause the steady disappearance of cellulose.

We therefore see, that these same processes may cause the disappearance of cellulose in soil and in waters, which plainly shows their great importance in the "self-purification", as also in the biological purification of sewage.

2. *The aerobic decomposition of cellulose by bacteria.*

In order to demonstrate denitrification in the presence of cellulose in the manner described above, a very small quantity of this substance (about 0,05%) only must be present, for on using more say, 2% the nature of the process is completely changed. This must be attributed to a strong decomposition of the cellulose by aërobic bacteria, which then takes place and which produces a large quantity of soluble organic matter, rendering the nitrification impossible. This last phenomenon may be best observed when use is made of the following culture medium:

Tapwater 100, paper 2, NH_4Cl 0,1, K_2HPO_4 0,05, chalk 2.

Instead of NH_4Cl we may also add KNO_2 (0,1), KNO_3 (0,1), peptone (0,1) or an unlimited quantity of MgNH_4PO_4 . The cultivation takes place at 28—35° in ERLÉNMEIJER flasks in a layer from 0,5—1 cm. in thickness, thus, under very aërobic conditions, so that on using KNO_2 or KNO_3 , no denitrification can be expected, at least not at the commencement.

If mud from a ditch is used as infecting material a decided growth is already noticed after 5 or 6 days, the cellulose turns to an orange colour and may even disintegrate to a thin paste after 3 or 4 weeks. Microscopically, we see, that we obtain besides the cellulose-dissolving bacteria a very rich accumulation of spirillae, which however do not themselves attack cellulose. I have often repeated these experiments and always with the same result: the cultures become extremely rich in spirillae and these consist of many varieties. As a rule different species were found in a same culture, large spirillae with several windings in company with small, very mobile ones, but sometimes it also happened, that it looked under the microscope, as if we were dealing with pure cultures of special spirillae. These different results being no doubt connected with the nature of the germs in the infecting materials employed. Often however, we meet besides the spirillae, infusoria, monads, amoebae and small forms of bacteria, sometimes also rod bacteria and spore forming organisms, but the spirillae are always in the majority.

If such cultures are transported into the same sterile medium, the chief character remains the same, but the growth takes place more rapidly and as a rule the number of species of spirillae is much reduced, so that frequently but a single one remains. Here it is perhaps the proper place to state, that an accumulation of spirillae may also be obtained in using a nutrient liquid composed as follows:

Tapwater 100, calcium lactate 2, peptone 0,05, K_2HPO_4 0,05,

which is infected with a small quantity of ditch-mud.

At temperatures from 28—37° exceedingly rich spirillae cultures are formed in this liquid. It would, however, be too rash thence to conclude, that lactate is formed as a transient decomposition product of the cellulose.

The destruction of the cellulose is not only apparent from the strong growth of microbes, but also from a microscopical examination of the fibres. As in the case of the denitrification process, these are here also found to be enveloped with a bacterial mucus in which is always found a very small rod-bacterium, and occasionally a large micrococcus, which itself does not attack cellulose, but much accelerates its dissolution by the small bacterium. The destruction is no doubt caused by the latter, for sometimes, we have obtained cultures, which exclusively contained this species only.

That the decomposition is here an aërobic one, is shown by the fact, that it commences at the surface of the culture and also takes place equally well when we cultivate in a very thin layer.

Owing to the dissolution of the cellulose the absorption of oxygen in the cultures may become so strong, particularly when working with thick layers of cellulose paste, that anaërobic processes become possible. If, now, nitrates or nitrites are still present in the culture denitrification will set in, but if these compounds are already decomposed, or if originally another source of nitrogen had been added, methane or hydrogen fermentation becomes possible. In the last case we microscopically observe the very characteristic rods with spores, accumulating on the fibres. In this anaërobic stadium the spirillae are for the greater part expelled but the destruction is now much more intense than when it took place exclusively under aërobic conditions so that in a short time the paper pulp gets for the greater part dissolved and leaves behind a bacterial mucus.

When using as infecting material soil, instead of mud from a ditch, we observe on the whole the same phenomena, only we do not find then that variety in species of spirillae noticed with ditch-water. As a rule a short, thick, granulated spirillum with one half winding is then conspicuous and I have succeeded in preparing pure cultures of this species, already observed previously ¹⁾.

An experiment with sea water showed, that this also causes the aerobic decomposition of cellulose and an accumulation of different species of spirillae was obtained at the same time. In this case the decomposition in the anaërobic stadium may also be caused by an anaërobic spore forming organism, which much resembles the bacteria of the methane and hydrogen fermentations but still presents a different shape.

I have tried to isolate the bacteria connected with the aërobic destruction but was not more successful than in the denitrification experiment. On sowing on broth-gelatin or broth-agar a number of bacteria species were found: *fluorescents*, *B. coli commune*, *B. subtilis*, *B. mesentericus* and several others unknown to me, but none of these species or none combination thereof was capable of attacking cellulose.

Our result that cellulose may be attacked by aërobic bacteria widely occurring in nature, is confirmed in a particularly convincing manner by the following experiment:

In a glass box are placed two discs of Swedish filterpaper between which has been sprinkled a little quantity of powdered $MgNH_4PO_4$; the paper is imbibed with a solution of 0.05 gram of K_2HPO_4 in 100 cc. of tapwater. If now we introduce upon the plate thus prepared a little

¹⁾ BEIJERINCK. Ueber oligonitrophile Microben. Centrbl. f. Bakt. Abt. II, 1901 Bd. 7, S. 574.

quantity of water containing in suspension humus, garden soil or, still better, ditch-mud, and if we cultivate at 24—28°, the paper gets covered after 4 or 5 days with yellowish-brown spots which, microscopically, are found to consist of bacteria. These spots spread with great rapidity, and it is highly interesting to observe how in a short time the white filterpaper is covered with the rusty culture. This is accompanied by a decided decomposition of the paper fibre, which is shown in the first place by the fact that the paper becomes quite soft and pulpy just on the spots exposed to the action of the brown bacterium, losing there all coherence and sinking down along the edges of the phosphate. The phenomenon becomes still more pronounced, when instead of filterpaper, linen or cotton is used; after about 10 days, the affected spots of the originally strong material have lost all power of resistance and after 15 days large holes will be formed when carefully pouring water on them.

Microscopically, it appears that a powerful destruction of the fibre is taking place (fig. 3) due to the action of a brown, very mobile, little rod bacterium (*Bacillus ferrugineus* fig. 4). The fibre is again enveloped by a mucus in which is found, in many cases, the same micrococcus as mentioned above (fig. 5 and 6). Owing to the combined action of these two bacteria the fibre may disappear completely and leave behind a mucus containing only micrococci; we then obtain an image as shown in fig. 7. In addition to amoebae and monads other small bacteria are found, but there is no question of the presence of anaërobics, which occur in the hydrogen or methane fermentations, the action being a purely aërobic one and taking place very well in filterpaper both sides of which are exposed to the air.

On transferring the brown spots to previously sterilised paper discs, between which $MgNH_4PO_4$ has been sprinkled and which have been saturated with a sterile 0,05% solution of K_2HPO_4 , the phenomenon remains constant. On inoculating them into the above described cellulose pulp a culture is obtained resembling that which arises by the direct action of ditch-mud or earth, but no spirallae are found this time, for these being microaerophilous cannot grow in the aërobic culture on the paper discs. On the other hand the cultures from paper pulp were occasionally capable of producing brown spots on paper discs, showing that in both cases the destruction of the cellulose may be caused by the same microbe. I also noticed a few times that the discs were covered with colorless spots caused by a larger mucus-secreting rod, and as moreover the paper pulp cultures often are only little colored, it must be assumed, that the aërobic

decomposition of cellulose may be caused by two microbes at least, but among these the brown pigment bacterium is the most conspicuous.

On using sea water as infecting material, similar brown spots were observed. When these were transferred to paper without addition of 3% NaCl they caused no destruction, which shows that we are dealing here with a specific sea bacterium.

I have made several experiments with various culture materials in order to isolate this very interesting cellulose-destroying brown pigment bacterium, which I was particularly anxious to accomplish after having observed, that the crude bacteria-mixture as grown on different culture media often again produces spots when spread over paper, which shows that on these media the said bacterium had kept alive. But I was again unsuccessful in isolating a species which either alone or in combination with other bacteria was capable of causing the brown spots on paper. Though I succeeded in isolating from these spots a brown and a yellow bacterium, which as a rule, were present in large numbers, yet, as in the case of the denitrification process, no destruction of cellulose could be induced by their pure cultures. The explanation of this circumstance has not yet been found.

The aerobic destruction of pure cellulose and also the more difficult destruction of the lignified cell walls,¹⁾ on which we cannot enter in this investigation, must, like the denitrification (which is only possible with non lignified cellulose and takes place out of contact with air) play an important part in the disappearance of vegetable substances in nature. The well known fact that wooden piles, when partly immersed in water are attacked exactly at the place of contact between the water and the air, the breaking of ropes, when suspended in water, exactly at its surface and also the aerobic decay of wood must be attributed mainly to the action of aerobic destroyers. VAN SEXUS (l. c. 103) who was acquainted with these facts, did not deny the possibility of a decomposition by aerobic bacteria but thought it very unlikely "as no phenomenon ever pointed to such a fact."

That the above-described yellowish-brown pigment bacterium plays indeed an important part in the disappearance of the cellulose, is shown by the following experiment.

On October 14, 1902 were buried in the garden of the bacteriological laboratory at about 15 c. m. below the surface a linen cloth with a red colored border, and in two other places four sheets of filterpaper, all in a horizontal position. Left in the soil untouched during the recent winter and on exhuming them March 22, 1903

¹⁾ The great stability of wood-cellulose towards microbial life is directly opposed to the ready decomposition of wood paper under chemical influences.

not a trace could be found of the filterpaper, whilst the linen cloth had become soft and pulpy, had lost all coherence and could only be removed from the soil in pieces; the red border, however, had retained its original structure. The originally white tissue had assumed the same yellowish-brown colour so familiar to me from the cultures on the paper discs, while on microscopical investigation the fibres appeared to be much decomposed and disintegrated into fibrillae and besides moulds and amoebae only small bacteria were observed. On putting some of the well-cleaned fibres on the paper discs prepared as described above, I obtained after three days the rapidly spreading, yellowish-brown spots of the destructive, small, rod-shaped pigment bacterium. A cellulose-destroying mould, *Mycogone puccinioides*, also could be isolated from the linen, but the fact that the yellowish-brown pigment bacterium was here predominant, could not be doubted.

3. *The decomposition of cellulose by moulds.*

The fact that cellulose may be attacked by certain fungi has been first stated by DE BARY¹⁾ for *Peziza sclerotium*, and the same was found by KISSLING²⁾ and by MARSHALL WARD³⁾ for a kind of *Botrytis*, by BEHRENS⁴⁾ for *Pseudodematophora*, *Botrytis vulgaris*, *Cladosporium herbarum* and *Aspergillus glaucus*. This last investigator did not notice any decomposition by *Mucor stolonifer*, *Penicillium glaucum* and *Penicillium luteum*. KOHNSTAMM⁵⁾ prepared a cellulose-destroying enzyme from *Merulius lacrymans* the common wood fungus. WENT⁶⁾ has shown, that *Monilia sitophila*, the "ontjom" mould from Java, is capable of digesting cellulose and KONING⁷⁾ has found that one of the

1) Ueber einige Sklerotien u. Sklerotienkrankheiten, Bot. Zeit. 1886, S. 377.

2) Zur Biologie der *Botrytis cinerea*, Diss. Dresden, 1889.

3) A lily disease, Annals of Botany, Vol. II, 1888/89, p. 346.

4) Tröckene u. nasse Fäule des Tabaks. Der „Dachbrand“, Zeitschr. f. Pflanzenkr. Bd. III, 1893, p. 84. — Untersuch. über den Wurzelschimmel der Reben, Centrbl. f. Bakt., Abt. II, Bd. 3, 1897, S. 584. — Beiträge zur Kenntniss der Obstfäulnis, Centrbl. f. Bakt. Abt. II, Bd. 4, 1898, S. 514. — Unters. über die Gewinn. der Hanffaser durch natürl. Röstmethoden, Centrbl. f. Bakt. Abt. II, Bd. 8, 1902, S. 114.

5) Amylytische, glucosidspaltende, proteolytische u. cellulose lösende Fermente in holzbewohnenden Pilzen. Beihefte z. Bot. Centrbl. Bd. 10, Heft 2, 1901., S. 90.

6) The influence of feeding on the secretion of enzymae by *Monilia sitophila*. Proc. Jan. 1901. — Ueber den Einfluss der Nahrung auf die Enzymbildung durch *Monilia sitophila* (Moxr) Sacc. Jahrb. f. wiss. Bot. Bd. 36, Heft 4, S. 643.

7) Genootschap ter Bev. v. Natuur- en Heelkunde Amsterdam, 2 series, dl. IV, Afd. 5, Zitting 7 Dec. 1901.

most common humus-inhabitants from the forest of Spanderswoude, *Trichoderma koningii*, possesses the same property.

We have succeeded in finding an experiment by means of which the cellulose-destroying moulds may be isolated from nature in a direct and certain manner. Two sterile discs of Swedish filterpaper are placed in a glass box and moistened with the following liquid:

Tapwater 100, NH_4NO_3 0,05, KH_2PO_4 0,05.

As infecting material earth or humus may be used, but the best results are obtained by simply exposing the opened box for about 12 hours to the open air. If then we cultivate at 24° and take care to keep the paper moist, colonies of moulds already become visible after 5 or 6 days, but it is only after 14 days or three weeks, that we notice the enormous richness of these cultures, and then we are surprised at the great number of mould species, which make their appearance. Many kinds which we seldom or never notice on malt-gelatin are found in large numbers on these paper discs. These species certainly are also capable of growing on malt-gelatin, but their germs, as they occur in nature, apparently find thereon an unfavorable soil. Another advantage of the cultivation on paper is that it is particularly favorable to the formation of perithecia and pycnidia, which do not readily develop on rich soils¹⁾.

From these culture experiments it appears that a continuous rain of spores from cellulose-destroying moulds falls in the garden as well as in the rooms of the bacteriological laboratory. For instance on March 11, when the weather was dry whilst the earth was moist, 152 cellulose-destroying moulds were collected on a plate of 275 c.m. square, after this had been exposed for 12 hours to the open air, and among these moulds about 35 species were recognised. As these germs must continually drop on the soil, it might be expected that the latter would be remarkably rich in living moulds and it appeared from experiments, that this is really the case at the surface of the garden soil, but in a much less degree than might have been expected, while lower down in the soil the number of moulds seems to be still less. From this it follows that most of the spores, which fall on the earth rapidly die off.

In order to prepare a pure culture of the fungi isolated by the "paper-experiment" some material from the raw cultures was transferred to malt-gelatin, where it appeared that the moulds were generally much contaminated with bacteria, from which however,

¹⁾ Compare MOLLIARD, Rôle des bactéries dans la production des périthèces des *Ascobolus*, C. R. t. 136, 1903, p. 899.

they could be freed by another inoculation. These bacteria are saprophytes which do not attack cellulose but grow at the expense of the products generated by the action of the moulds on cellulose. This result was not unexpected for, as stated in the preceding paragraph, the cellulose-destroying bacteria live in a faintly alkaline medium, whilst in the case of moulds the reaction is acid, owing to the presence of KH_2PO_4 . In order to be perfectly certain of the pureness of the moulds, cultures from the spores were finally made on malt-gelatin.

The following species, which were detected in these cultures, have been submitted to a closer examination:

1. *Sordaria humicola* OUD.
2. *Pyronema confluens* TEL.
3. *Chaetomium kunzeanum* ZOPF.
4. *Pyrenochaeta humicola* OUD.
5. *Chaetomella horrida* OUD.
6. *Trichocladium asperum* HARZ.
7. *Stachybotrys alternans* OUD.
8. *Sporotrichum bombycinum* (CORDA) RABH.
9. " *roseolum* OUD. en BELJER.
10. " *griseolum* OUD.
11. *Botrytis vulgaris* FR.
12. *Mycogone puccinioïdes* (PREUSS) SACC.
13. *Stemphylium macrosporoïdeum* (B. en BR.) SACC.
14. *Cladosporium herbarum* (PERS.) LINK.
15. *Epicoccum purpurascens*. EHRENB.

In the determination of these species, of which Nos. 9¹⁾ and 4, are new, we have been kindly assisted by Prof. Dr. C. A. J. A. OUDEMANS, to whom we have to express our thanks.

In order to form an opinion on the destruction of cellulose by the isolated species, and also to study their fructification, pure cultures were inoculated on paper discs, which after sterilisation, were drenched with the above-named solution. Instead of merely placing the spores on the paper, it was found desirable to push them in it by means of a platinum wire and then to reduce the spots there to pulp. The cultivation is made at 24[°], care being taken to keep the paper moist, for which it was found advantageous not to use water only but the said liquid, as the nitrogen in particular is rapidly used up. The above-named moulds all grow over the paper discs, form their fructification-organs in a very characteristic manner and often produce intensively colored, brown, black and red pigments, which are absorbed by the paper

1) Nederl. Kruidkundig Archief, Januari, 1903.

fibre. Interesting are the cultures obtained in this way of *Chaetomium kunzeanum*, which sometimes produces a carmine-red pigment and which forms dark red peritheciae, the asci of which contain eight grey spores; those of *Chaetomella horrida*, which forms delicate black hairy pyrenidiae, and particularly those of *Pyrenochaeta humicola*, which produces an intense black pigment, stable towards acids and alkalis, and which communicates a dark colour to the fibres, quite resembling the humus coloring matters. This latter species however, grew more readily on an alkaline medium, so that we preferred in this case the said drenched paper discs, between which $Mg NH_4 PO_4$ had been sprinkled. An interesting culture is also that of *Sordaria humicola*, as this ascomycete is only then capable of forming perithecia on paper discs, when these give no longer any reaction on ammonia or nitrates. Besides the above-named species, a luxurious growth was obtained of *Trichocladium asperum*, *Mycogone puccinioides* and *Stemphylium macrosporoides*, which three species exhibit great similarity both in their morphological and physiological properties. *Epicoccum purpurascens* also grew strongly on the paper and formed a purple-red pigment. This species I met several times in the air and also (in company with *Cladosporium herbarum*) on half decayed leaves of *Populus balsamifera*.

Cultures of these moulds were not only made on paper discs, but also on cellulose in ERLIXMEYER flasks, into which was introduced a thin layer of the following culture liquid:

Tapwater 100, paper-pulp 2, $NH_4 NO_3$ 0,05, $KH_2 PO_4$ 0,05.

In this case a repeated addition of $NH_4 NO_3$ proved very advantageous. On the pulp the cellulose-destroyers grow still better than on the paper discs and in 3 or 4 days the cellulose is converted by the mycelium into a coherent mass. Afterwards, the fructification organs appear, and with *Botrytis vulgaris* even formation of sclerotia was observed.

The destruction of the cellulose may be regarded as certain when strong growth on the paper discs and on the paper pulp are being observed. The impurities contained in the paper may also cause a slight growth of moulds which do not attack cellulose, but these soon cease to develop. The decomposition may be seen very clearly by a microscopic examination of the cultures on filter-paper, when these have stood a long time. It will then strike us how a large number of fibres have suffered a process of dissolution; sometimes pores are formed perpendicularly to the direction of the fibre, sometimes the fibres have disintegrated into fibrillae. Fig. 9

of our illustration shows the image of the destruction by *Mycogone puccinioides*, in which the structure of the fibrillae and the said pores are visible.

The degree of destruction also may be ascertained by direct weighing. A culture with *Mycogone puccinioides* was made on a double disc of filterpaper, two equally heavy filters serving as control. After a culture, lasting 40 days, the discs, from which the strongly developed mycelium was not removed, weighed 1.00 gram, whilst the controlling discs weighed 1.16 gram, showing that about 14% of the cellulose had disappeared. A similar experiment with *Trichocladium asperum* gave a loss of 9%. These great losses only can be explained by the oxidation of the products derived from the cellulose under the influence of the respiration process. The oxidation of cellulose also was studied with filterpaper pulp, namely by weighing the amount of carbon dioxide, liberated during a culture of *Chaetomium kunzeanum*. In this experiment an oxidation of about 4% of the cellulose could be noticed after a 28 days culture, a quantity large enough to remove all doubt about the destruction of the cellulose.

No, growth or only a very small one, was observed when cultivating the moulds on:

Tapwater 100, agar 2, NH_4NO_3 0,05, KH_2PO_4 0,05,

but as soon as cellulose was added a strong development set in, showing in a surprising manner, that agar is a less nutrient food for these moulds than cellulose. The cellulose used in these experiments must be very finely divided and was prepared by treating cottonwool with concentrated hydrochloric acid, which causes the cotton fibres to break up into very small fragments. A preparation, which appeared to be still more suitable was prepared as follows: Paper which has been converted into soda-cellulose by the action of strong soda-lye, is readily soluble in sodium xanthogenate to a light yellow liquid: the "viscose" of CROSS and BEVAN¹⁾, which is purified by precipitation with alcohol; on adding hydrochloric acid to its aqueous solution cellulose is precipitated in a very pure condition. I have to thank MR. DE JONGH SCHEFFER, for a specimen of this preparation, which he prepared in the chemical laboratory of the Polytechnic School at Delft.

I found that, when cultivating on this agar-cellulose, the growth entirely depends on the quantity of the cellulose added: with much cellulose a strong growth was observed.

¹⁾ CROSS and BEVAN, *Cellulose*, 1895, p. 25. London, Longman Green and Co.

As in the case of the moulds investigated by the above-named observers, also the species employed by me showed the presence of an enzyme, which dissolves cellulose and to which the name of "cellulase" may be given ¹⁾. If cultures on cellulose pulp were treated with chloroform, the liquid, after being freed from chloroform by evaporation, appeared capable of reducing FEHLING's copper solution. If the culture had been boiled before being treated with chloroform, no reduction took place. From these last experiments, which were conducted similarly to those of BEHRENS (l.c.), it appears that the moulds only produce the quantity of reducing matter necessary for their growth and no more. That the quantity or the nature of the enzyme secreted by the moulds differs considerably, is shown by the great difference in destructive power, as may be readily observed from the growth on the paper discs and from the dissolution of the cellulose in the paper-pulp cultures. To the powerful destroyers belong: *Trichocladium asperum*, *Mycogone puccinioides*, *Stemphylium macrosporoïdeum*, *Chaetomella horrida*, *Botrytis vulgaris*, *Epicoccum purpurascens*. To the moderately strong ones: *Chaetomium kunzeanum*, *Stachybotrys alternans*, *Cladosporium herbarum*, *Pyrenochaeta humicola*, *Pyronema confluens*. To the weak ones: *Sordaria humicola*, *Sporotrichum bombycinum*, *Sp. roseolum*, *Sp. griseolum* and *Aspergillus niger*. No destruction was noticed with *Mucor stolonifer*, *Mucor mucedo*, *Dematium pululans* and *Rizopus oryzae*.

Summary of results.

1. Cellulose may be made to dissolve by the action of denitrifying, non-sporeforming aërobic bacteria provided there be an *limited* supply of air.
2. Although nitrification cannot take place in the presence of a somewhat large quantity of soluble organic matter, cellulose does not affect this process in case of sufficient aëration.
3. The combined action of nitrification and denitrification must play an important part in the disappearance of cellulose in nature, for instance in the self purification of waters and of the soil, as also in the biological purification of sewage.

¹⁾ This name, already used by KONSTAMM (l.c.) is preferable to the name *cytase* which has been used by BROWX and MORRIS (Journal of Chem. Soc. 57, 1890, p. 458) for the cellulose-dissolving enzyme in germinating seeds and should according to METSCHNIKOFF (Ann. Inst. Pasteur, 1899, t. 12, p. 737) be given to an alexin occurring in normal serum.



4. Cellulose may also be attacked, when there is a full supply of air by widely distributed, aërobic, non-sporeforming bacteria, among which a brown pigment bacterium (*B. ferrugineus*) is predominant. The destruction is particularly strong in symbiosis with a yellow micrococcus, which itself is inert.

5. Extraordinarily rich spirillae cultures are formed in nutrient liquids in which cellulose is being attacked by aërobic bacteria after infection with ditch-mud or garden soil. Probably the distribution of the spirillae in nature is mainly governed by cellulose.

6. The property of moulds to attack cellulose is a very common one. The dissolution is due to a specific enzyme to which the name of "cellulase" may be given.

7. One of the causes of the origin of humus coloring matters is the formation of pigments from cellulose by bacteria and moulds. This investigation has been made in the bacteriological laboratory of the Polytechnic School under the guidance of Prof. BEJERINCK.

Delft, March 1903.

EXPLANATION OF THE FIGURES.

Fig. 1. Fibre of filterpaper with denitrifying bacteria, disintegrated into fibrillae, enclosed in mucus. Enlargement 550.

Fig. 2. Debris of filterpaper at the end of the denitrification process, most of the fibres are dissolved. α the last debris of cellulose fibres, β , γ and δ nonattacked elements of "woodcellulose". Enl. 100.

Fig. 3. Fibre of filterpaper with aërobic bacteria disintegrated into fibrillae, enclosed in mucus. Enl. 550.

Fig. 4. Bacterium from the preceding figure more strongly enlarged; arrows represent motion. Enl. 1500.

Fig. 5. Fibre of filterpaper attacked by an aërobic bacterium with saprophytic micrococcus, commencing to disintegrate into fibrillae. Enl. 550.

Fig. 6. Two fibrillae of the preceding fibre more strongly enlarged, with α aërobic destructive bacteria and β saprophytic micrococcus. Enl. 1500.

Fig. 7. End of the destruction in fig. 5 the fibrillae having become invisible; micrococci only visible. Enl. 550.

Fig. 8. Fibre attacked by aërobic bacteria, disintegrating into fibrillae and enclosed in a thin mucous layer as medium for a spirillae culture in which 3 species are recognisable. Enl. 550.

Fig. 9. Destruction of a fibre of filterpaper by *Mycogone puccinioides*, besides the fibrillary structure, cross pores have been formed in the fibrillae owing to the action of the cellulase. Enl. 550.

(May 27, 1903).



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