PROCEEDINGS OF THE
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In de Proceedings:
Vol. XXI, p. 836, line 3 from the top, *read* Supplement N°. 42*e*
for Supplement N°. 43*a*.

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CONTENTS.

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PROCEEDINGS

VOLUME XXI

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CONTENTS.

Botany. — "*On the influence of electrolytes on the motility of Chlamydomonas variabilis Dangeard*". By C. Spruit P.Pzn. (Communicated by Prof. Went).

The reactions of unicellular motile organisms to external stimuli are not always equally prompt. We speak of "condition", probably due to one or more of these incalculable factors which make experiments with living organisms so troublesome.

In the case of *Chlamydomonas variabilis Dangeard* I have found that the case of response of this unicellular, motile green Alga to light, gravity or chemotactic stimuli depends not only on the nature of the dissolved substance, but also on its concentration. By systematic investigation of the motility of the Alga in solutions of a few salts, an attempt has been made to obtain some idea of the manner in which electrolytes influence this phenomenon. Although it would have been desirable to investigate the influence of numerous electrolytes, it has nevertheless become clear from the data collected hitherto, that the action of electrolytes on the motility of *Chlamydomonas* agrees in many respects with their action on the solution and precipitation of colloids.

A culture method, indicated by Jacobsen [1]), was employed in order to make large quantities of *Chlamydomonas* species available.

After cultures had been obtained continuously for some months by inoculation, the experiments were undertaken. Part of each culture employed was fixed with formalin. Determination showed that the cultures always contained almost exclusively individuals of *Chlamydomonas variabilis Dangeard*.

Under favourable conditions this species is sensitive to light, to gravity and to some chemotactic stimuli. Under certain conditions the Alga reacts also to contact, by attaching itself to solid objects. In the experiments *Chlamydomonas* generally reacts negatively to light, sometimes a positive reaction is observed. The latter was more frequently the case if the alga remained in the culture fluid.

Under the influence of gravity an obvious and rapid positive

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[1]) H. C. Jacobsen. Zeitschr. f. Bot. Bd. II 1910.

reaction was noticed (positive geotaxis), whereas in the literature *Chlamydomonas pulvisculus* is stated to have a negative geotactic reaction. Very dilute acids and phosphates were found to be positive chemotactics for *Chlamydomonas*. The alga reacted with negative geotaxis to more concentrated acid solutions and to bases.

All these reactions were clearly observed with the alga in distilled water. Addition of small quantities of acid and base caused the reactivity to decrease. Above a certain concentration no reaction occurred. It could be observed microscopically that in such cases the motility was greatly diminished. The reactivity and motility could also be decreased by adding salts. The concentrations for salts were greater than for acids .and bases, but nevertheless still small.

Increase of electrolyte concentration (whether by addition of acid, base, salts or combinations of these) diminished the sensitiveness to light, to gravity and to chemotactics to an approximately equal extent. By means of the reactions indicated the influence of electrolytes on the motility of the alga was investigated.

It was very easy to separate the individuals of *Chlamydomonas* from the culture-fluid. For this purpose the fact was utilized that in cultures sufficiently dense for experiments, the alga was in such a condition that it readily attached itself to solid bodies. A glass tube of about 0.5 c.m. diameter, sealed at its lower end more or less to a point, was filled with the culture fluid. The tube was placed vertically in unilateral diffuse daylight. After five minutes a green band of algae was visible at one side of the tube. In this condition the motility is still so great that the algae all swim to one side of the tube, where they come into contact with its wall. In consequence of this contact they had fastened themselves to the glass. They were so firmly attached that it was possible to suck out the culture fluid with a pipette while the algae remained sticking to the wall. Next a quantity of distilled water was introduced into the tube, which was then shaken to distribute the algae in the water. The tube was again placed in a vertical position and exposed to unilateral diffuse daylight. Under the influence of the distilled water the algae showed not the slightest tendency to attach themselves. The light indeed caused them to collect on one side of the tube as a dense green band, but under the influence of gravity the algae constituting this band soon moved to the bottom, so that after five minutes there was a distinct accumulation at the lower end.

By means of a pipette the water could now be removed almost completely. After this preparation of the algae the solution of which the effect was to be investigated, was introduced into the tube.

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From what was said above p. 783 line 15 it may be deduced that it (practically) makes no difference, whether the reaction to light, or to gravity or to chemotactics is employed to judge the motility of *Chlamydomonas*. A reaction was sought which could easily be followed macroscopically. The gravitational one was found to be the most suitable, for it was easy to ascertain, whether the alga definitely moved towards the bottom, or whether the motility was so small, that there was no question of a downward movement. In the former case a definite accumulation was soon formed at the bottom of the vertical tube; in the latter case no clear accumulation was observed. The result of the experiment was always noted after *ten minutes*.

According as the algae reacted to gravity, or not, it was possible to ascertain, whether the motility in a given solution was fairly large or very small. In all solutions in which the alga reacted to gravity the motility was not uniformly great; nor was this the case in those solutions, in which no reaction could be observed. We could, however, determine the limiting concentrations at which the reaction to gravity still occurred and at which it could no longer be observed. By making a series of salt solutions of increasing concentrations in distilled water, it was possible to determine the concentration of the salt at which a reaction was still just observable and that, at which a reaction no longer occurred. The concentrations between these two limits may be called transitional concentrations. The mean of the two limits we may regard as the concentration, at which, at least theoretically, the transition took place from a condition of motility in which the reaction to gravity occurred, to a condition of motility in which the reaction no longer took place. This concentration we call the *critical transitional concentration* or the *critical concentration*.

For solutions in which the salt concentration was constant, whilst the H·-ion concentration increased regularly, we similarly speak of the limiting and of the critical concentrations.

The values of the limiting concentrations become much more certain by making each experiment six times. As the two limiting concentrations we regarded that one, at which all six tubes showed a definite accumulation and that one, at which no accumulation occurred in any of the tubes. Concentrations at which a positive reaction was found in some only of the six tubes, were regarded as transitional and were left out of account.

In order to obtain a clear picture of the influence of a salt we must pay attention to the H·-ion concentration of the solution. The solutions which were employed in investigating the effect of a given

salt, not only varied in a regular manner as regards concentration of the salt, but the degree of acidity was also varied regularly. The hydrions are the cause of the effect which small quantities of acids exert on *Chlamydomonas*. The effect of small quantities of basis is due to hydroxyl ions.

The product of the H-ions and the OH'-ions is constant in aqueous solution at any given temperature. Hence the strength of an alkaline solution can be expressed by the H·-ion concentration.

We now proceeded as follows. First the critical concentration was determined for solutions of a given salt in distilled water. Then the same was done for solutions of the salt containing 0.00005 n. acid, and next for those containing 0.00010 n. acid, etc. Finally small quantities of base were added to the salt solutions in order to determine in the same way the limiting concentrations and the critical concentration for series of solutions which were feebly basic instead of feebly acidic.

Since the effect of electrolytes is due to the ions, it was necessary to ensure that a regular variation of ionic concentration was indeed obtained by the procedure outlined. With regard to the ions of salts there need be no doubt, but for the hydrions this was not self-evident.

The hydrion concentration of 0.00005 n. sulphuric acid for instance, is in practice not always equally great. It was possible, by adding small quantities of acid or base, to obtain regularly increasing or decreasing H·-ion concentrations by following the following directions. The solutions of a salt were made acid or alkaline by addition of the acid or the base, which had an anion or a cation in common with the salt (a sulphate was therefore acidified with sulphuric acid, a potassium salt was made alkaline with potassium hydroxide). All acid solutions of a salt were prepared with the same solution of an acid and likewise all alkaline solutions with the same solution of a base. Newly distilled water was always used.

Although a regular variation of H·-ion-concentration was thus obtained, its absolute value was unknown. Nor was it possible to compare mutually the H·-ion concentration, and therefore the degree of acidity, of solutions acidified with hydrochloric and sulphuric acids.

For solutions of sodium acetate at different H·-ion concentrations the absolute value was determined electrometrically. These solutions contained sodium acetate and acetic acid. The solutions were again employed in series, and in each series the concentration of the sodium acetate varied in a regular manner. By paying attention to the relation of the acetate concentration to that of the free acetic

acid, it was possible to ensure that in each series the H·-ion concentration remained approximately constant, while for the various series the H·-ion concentration varied in a regular manner. Of the solutions containing the limiting concentrations of sodium acetate, the H·-ion concentration was now determined electrometrically.

Mixtures of sodium acetate and acetic acid have a H·-ion concentration which in practice is well defined, can be calculated in advance and can moreover be readily determined electrometrically. These mixtures are "buffer solutions".

The experiments were carried out at room temperature. The literature indicated that in so far as the influence of temperature on chemotaxis has been investigated at all, it is insignificant. Nor has a great influence of temperature on certain phenomena of colloidal chemistry, e. g. on the stability of suspensoids, been recorded.

For a series of solutions of carbonic acid in tap water the limiting concentrations were determined at 25° C. and at about 0° C. For both temperatures the same result was obtained. Nevertheless the temperature was always noted.

We always worked in diffuse daylight. An attempt to carry out the experiments in the dark was unsuccessful, as it yielded very irregular results.

The limiting concentrations observed and the critical concentrations calculated from them were plotted graphically for each of the salts investigated.

On the abscissa-axis of a biaxial system of rectangular coördinates the concentration of the salt was plotted, and on the ordinate axis on one side of the origin the concentration of the acid, on the other side that of the base. For mixtures of sodium acetate and acetic acid the acidity was indicated by plotting the H·-ion concentration on the axis of ordinates.

The limiting concentration at which the reaction to gravity still just occurred was indicated by, the limit at which no reaction was visible by °. The points found for the critical transitional concentration by calculation, were connected by a curve, which was regarded as the boundary between the region containing all concentrations of salt and base, and of salt and acid, at which the gravitational reaction took place, and the region of concentrations, in which no clear reaction occurred.

Figures 1, 2, 3, and 4 reproduce the curves for K_2SO_4, sodium acetate, KNO_3 and KCl, at least in so far as they have been determined.

In order to prove that the effect of acid and base was due to

the H·-ion concentration of the solution, a series of solutions was prepared, which all contained 0.01 normal sodium acetate, but varying quantities of free acetic acid or free sodium hydroxide. We thus obtained series of solutions in which the concentration of the acetate was constant, while that of the H·-ions varied gradually. The concentration of the other constituents of these solutions was too small for them to have any significance.

It was now found, that the reaction to gravity did not take place at all or took place badly in the most acid and in the most alkaline solutions of the series. The H·-ion concentration of the limiting solutions was measured electrometrically and was found to be for acid solutions between $[H·] = 10^{-5.9}$ and $[H·] = 10^{-5.5}$ (the H·-ion concentration was expressed in gramions per litre), and for alkaline solutions between $[H·] = 10^{-10.7}$ and $[H·] = 10^{-11.2}$. We may assume that, in this case at least, the effect of acid and base is to be attributed for the most part to the H·-ion (or OH'-ion) content.

The same experiment was repeated with solutions containing instead of acetic acid and an acetate, malic acid and a malate (these solutions always contained 0.01 grammolecules per litre of sodium malate). For acid solutions the limit was here found to be between $[H·] = 10^{-5.1}$ and $[H·] = 10^{-4.9}$ and for alkaline solutions between $[H·] = 10^{-10.6}$ and $[H·] = 10^{-11.1}$. These results confirmed the conception of the influence of the H·-ions. The displacement of the limits in acid malate solutions with respect to those of acid acetate solutions showed, however, that even small concentrations of salt also contribute to the effect.

In order that enough observations could be made to give an idea of the behaviour of the alga in solutions of a single salt, it was often necessary to use a fresh culture. In that case the last determinations with tle old culture were repeated with the new one. Often the results were not completely identical, but the differences between the two cultures were generally so small, than they could be neglected. In the experiments with KCl, however, once a great displacement of the limiting concentration was observed on using a fresh culture. Figure 3 shows how in solutions containing in addition to KCl, 0.00065 normal KOH, the new culture showed a modified behaviour. In consequence of this the curve consists of two discontinuous pieces. It is probable that the new piece would indeed be a continuation of the old, if we displace the new piece in a horizontal as well as in a vertical direction. The dotted lines would then probably unite the portions of the two pieces which correspond. In using new cultures with sodium acetate a less pronounced dis-

continuity was found. The portions I, II and III were each obtained with individuals from a different culture.

The cause of the different behaviour of the cultures is probably to be found in the fact, that the nutrient solution for the cultures had not the same composition when used. The plasma colloids probably form compounds with acids and bases and adsorb all kinds of ions. If the nutrient solution were not of the same composition, then the behaviour of the plasma colloids (and it was probably these colloids that were affected by the electrolyte solutions) need not be constant. That the fluid from the cultures had not always the same composition was pretty certain.

Fig. 1.

The treatment of the alga, before it was used in the experiment (compare p. 783) was such that only the culture fluid was removed completely. That the treatment removed substances from the organisms themselves, is not probable. But this must have been the case, when the washing in distilled water lasted longer than half an hour. In that case the sensitiveness to electrolyte solutions was greatly increased.

Only the curve for potassium sulphate is quite complete [1]. The course of this curve is, for the most acid solutions (from 0.00015 n. H_2SO_4) onwards, quite different from that for the most alkaline solutions starting (from 0,00100 n. KOH). In the latter case we can understand the course, if we suppose, that the effect of the salt and of the OH'-ion is more or less additive. For the behav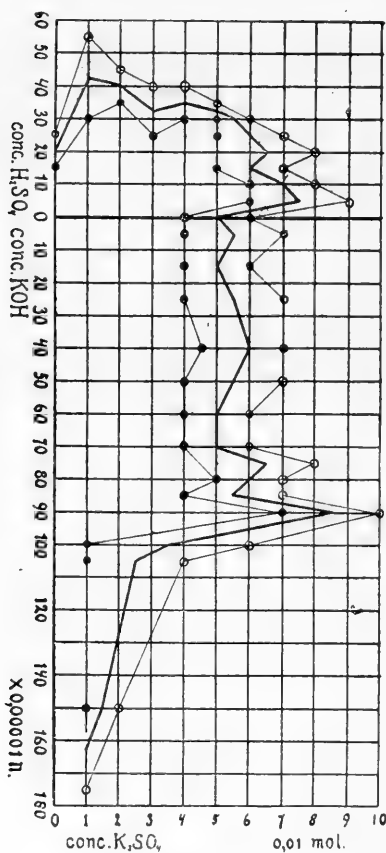iour of potassium sulphate in company of H·-ions (acid) there is no question of addition. If we follow the curve in the acid solutions, starting from the ordinate-axis, we see that the curve at first enters higher into the acid region, i.e. that small quantities of salt brought

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[1] For the most acid solutions the critical concentration was determined according to the content of acid.

about that a greater H·-ion concentration can be tolerated. After the concentration of the sulphate has become 0.02 normal, the curve recedes again and later on makes another bend (to 0.00015 n. H_2SO_4, 0.12 n. K_2SO_4), which we may consider due to the H·-ions counteracting somewhat the effect of the salt in this portion of the curve.

The course of the curve for sodium acetate (fig. 2) is in the most acid solutions (from about $[H·] = 10^{-5.2}$ to $[H·] = 10^{-6.4}$) of the same
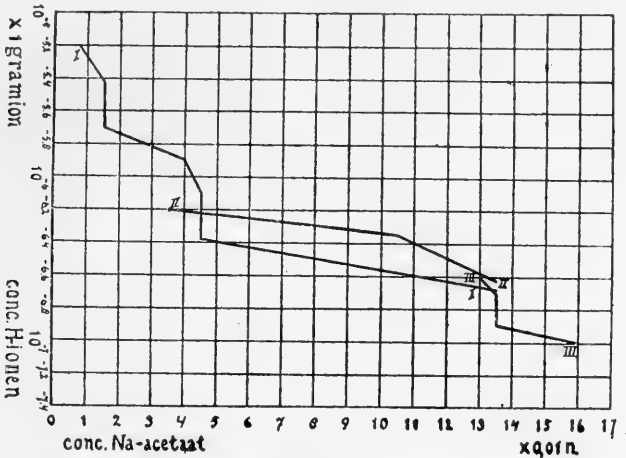
Fig. 2.

nature as that of the curve for K_2SO_4 in the most acid solutions. It was not possible to indicate this H·-ion concentration for the place, where the curve reaches the ordinate-axis. In so far as the curve has been indicated in this portion, we likewise see two bends; the first is caused by small quantities of acetate counteracting the effect of the H·-ions, while the second is again brought about by the H·-ions diminishing the effect of the salt.

That the influence of base and of salt was approximately additive, while acid and salt interfere with each other's action, is an important phenomenon.

The same phenomenon was observed by HARDY [1]) in flocculation and solution of globulins in acid and alkaline salt solutions. The globulins form colloidal solutions, which in their behaviour towards acids and bases, must be reckoned among the emulsoids. For they are colloids, which are positively charged in acid and negatively in alkaline solution, because they are ampholytes, i.e. substances which behave both as acids and as bases.

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[1]) W. B. HARDY, Journ. of Physiol., Vol. XXXIII, 1905—06.

Probably in close connection with the behaviour of globulins in acid and in alkaline solutions is the fact that the acid concentration at which the globulins went into solution, is very dependent on the nature of the salt present in solution, while the concentration of alkali is much less influenced thereby, if at all. This also was shown by HARDY.

A corresponding peculiarity came to light in our experiments on the motility of *Chlamydomonas*. We found that the acid concentration in acid malate solutions was displaced in relation to that in acid acetate solutions, whereas the alkali concentration in malate solutions was not so displaced in relation to that in acetate solution (see p. 787).

In so far as concerns its motility with regard to acid, base, a c i d i c and alkaline salt solutions, the behaviour of *Chlamydomonas* therefore showed a striking correspondence to the behaviour of emulsoid solutions of globulins with regard to the same reagents. We may therefore suppose, that the motility of *Chlamydomonas* under the influence of acid and alkaline salt solutions, depends on a colloidal-chemical change of the cell, most probably of the protoplasm. This hypothesis is not wholly unexpected. Protoplasm is generally regarded as a colloidal mass. According to our observations the plasma colloids would show some of the properties of emulsoids. After having observed the correspondence between the effect of a c i d and of a l k a l i n e solutions on the motility of *Chlamydomonas* and their effect on the emulsoid globulins, we will next try to as certain whether the influence of s a l t s [1] on the motility of the alga shows any agreement with their action on emulsoids or indeed on suspensoids. For this purpose we must examine the portion of the curve for K_2SO_4 between 0.00015 n. H_2SO_4 and 0,00100 n. KOH (fig. 1) and also the curves for KCl (fig. 4) and for KNO_3 (fig. 3) in so far as they are plotted.
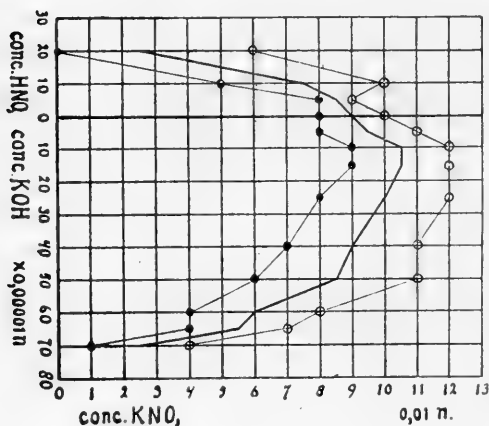
Fig. 3.

These portions of the curves differ somewhat in shape. For KNO_3

[1] We suppose that in the portions of the curves now to be discussed, the influence of the salt predominates, while in the portions which have already been dealt with the influence of acid and base was more prominent.

the course is the simplest; for K_2SO_4 it is the most capricious. In one respect they agree, in that they are approximately symmetrical on either side of a horizontal line, which for KNO_3 lies at about
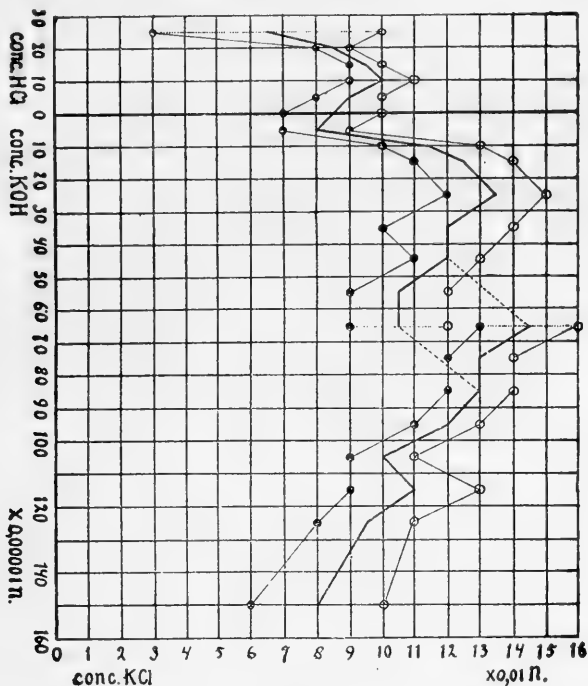
Fig. 4.

0.00035 n. KOH (fig. 3), for KCl perhaps at 0.00045 n. KOH (fig. 4) and for K_2SO_4 at 0.0040 n. KOH (fig. 1), although the axis of symmetry for KNO_3 and for KCl is not horizontal. This symmetry is too striking to be neglected, especially in the case of KNO_3 (fig. 3) and of K_2SO_4 (fig. 1). It seems to me an indication that the irregularity in this portion of the curves is not caused by experimental errors; moreover the sixfold repetition of the experiments also warrants this.

The symmetry was probably caused by the salts being active both with their cations and their anions. The part played by anions and cations, when the plasma colloids were positive, was probably reversed when the colloids were charged negatively.

The complication in the course of the curves consists in the presence of maxima; with K_2SO_4 (fig. 1) clearly five such may be distinguished, one at 0.00040 n. KOH and then two on either side; at 0.00075 n. KOH and at 0.00005 n. KOH there is in each case a low summit, at 0.00090 n. KOH and at 0.00005 n. H_2SO_4 a high one. In the case of KCl (fig. 4) there are perhaps also five. A con-

sideration of the curve for KNO_3 seems to indicate at first only a single large maximum at about 0.00030 n. KOH, but when we fix our attention on the course of the lines joining the limiting concentrations, we find that there are really five apices, namely at 0.00010 n. HNO_3, at 0.00010 n. KOH, at 0.00030 n. KOH, at 0.00050 n. KOH and at 0,00065 n. KOH. They are arranged very symmetrically on either side of a middle axis.

I have found nothing in colloidal chemical literature permitting of a direct comparison with our case. Perhaps the reason is that the behaviour of colloids towards salt solutions at various H·-ion concentrations has generally not been examined systematically, or where this was done, the quantities of acid and base added were much larger.

Nevertheless the occurrence of these summits is not in conflict with present views on the behaviour of amphoteric colloids. The proteins for instance might be able to combine with one or with more molecules of acid or base. In this way compounds might be formed which could behave very differently towards salts. No agreement has been reached about the conditions determining the existence of these various protein-acid and protein-base compounds. T. B. ROBERTSON [1]), however, considers that he has proved that their stability is exclusively determined by the H·-ion concentration of the solution. If this view is correct, then the presence of the summits in our curves might perhaps be susceptible of explanation.

The concentrations, in which the salts acted, were small. The highest amount was found for $Ca(NO_3)_2$, i.e. 0.40 normal. Very small values were found for phosphate. For binary electrolytes the concentrations were 0.10—0.20 normal. The greatest contrast was formed by plurivalent cations and plurivalent anions (calcium salt-phosphate).

We can also deduce something from figures 1, 3, and 4 about the different behaviour of univalent and plurivalent ions. The curve for potassium sulphate (fig. 1) has a vertical direction between 0.00015 n. H_2SO_4 and 0.00100 n. KOH. Here we have a bivalent anion together with a univalent cation; the curves for KCl (fig. 4) and KNO_3 (fig. 3) run obliquely downwards to the left. Here there is a univalent cation with a univalent anion. Experiments which were made with $Ca(NO_3)_2$, showed clearly that the curve which might be plotted from it, would be still much more oblique, but in the same direction as that for KCl and KNO_3. In this case a bivalent cation accompanies a univalent anion. If the direction is

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[1]) T. B. ROBERTSON, Die Physikalische Chemie der Proteïne. Dresden 1912.

related to the ionic valency of the salt, then the order $K_2SO_4 - KCl$ and $KNO_3 — Ca(NO_3)_2$ which has been found, is explicable.

It is further remarkable, that the curve for K_2SO_4 (fig. 1) reaches so far into the alkaline region, while the curve which might have been plotted for $Ca(NO_3)_2$ [1] would chiefly come to lie in the acid region.

The influence of the small salt concentrations, as well as that of ionic valency point to a possible correspondence between the processes which occur in the change of motility of *Chlamydomonas* and the process of the flocculation of suspensoids.

The influence of salts on the condition of emulsoids often suggests an arrangement of the ions in definite series. For the anions there is the series of HOFMEISTER. In a process, occurring in accordance with these ionic series, the influence of the salts is said to be lyotropic.

It was therefore desirable to see, whether the influence of salts on the motility of *Chlamydomonas* is one according to the lyotropic series. This was only investigated for the anions. For algae from one and the same culture the following series was found:

$$KI < KNO_3 < KCl < KBr, KCNS.$$

This was by no means the order of anions, if the influence of the salts had been lyotropic, for then it would have been

$$KCl < KNO_3 < KBr < KI < KCNS.$$

We must not attach too much value to this result. The ionic series is reversed, when the medium becomes acid instead of alkaline, while in neutral solutions transitions between the alkaline and the acid series are found.

The observations on *Chlamydomonas* were carried out at 0.00015 n. KOH, where there was accordingly much chance of finding one of the transitional series. We were, however, obliged to work in very feebly alkaline solutions, because at a different degree of acidity we should be comparing for the various salts such concentrations as were not, according to the curves, really comparable. In that case we should have compared a maximum for one salt with a minimum for another salt. In reality a good comparison would only be obtained for concentrations of a specified maximum, e.g. the middle one, for each of the salts.

In any case we can say with some probability that the action of

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[1] The concentrations of the solutions change each time by 0.05 n.; for this reason the results were not sufficiently accurate for a curve to be traced.

the salts on *Chlamydomonas* might suggest a comparison with suspensoids rather than with emulsoids.

In this respect also there is a correspondence between the phenomena studied in *Chlamydomonas* and the processes which occur in the colloidal globulins. These also were flocculated by small quantities of salts in HARDY's experiments and the valency of the ions played an important part.

The globulins may be reckoned among the emulsoids on account of their behaviour towards base and acid, but the effect of salts leads to the conclusion, that they are emulsoids possessing certain suspensoid properties.

We might conclude from our experiments, that the power of *Chlamydomonas variabilis* to react to gravity, (to light and to chemotactica) is influenced by electrolytes in such a manner, that there is much analogy to the action of electrolytes in the flocculation and solution of colloids. For this reason the hypothesis is possible, that in *Chlamydomonas* we are concerned with an action of the electrolytes on the colloids of the protoplasm. These colloids would then behave in such a way towards acid, base and salt, that a comparison with the behaviour of globulins (as observed by HARDY) was the most plausible. The plasma colloids would be emulsoid substances with some suspensoid properties.

Delft, November 1918.

Laboratory of Technical Botany.

Geology. — *"On the Non-existence of Active Volcanoes between Pantar and Dammer (East-Indian archipelago), in Connection with the Tectonic Movements in this Region"*. By Prof. H. A. Brouwer. (Communicated by Prof. G. A. F. Molengraaff).

(Communicated in the meeting of January 27, 1917.)

It is a striking phenomenon that active volcanoes occur in all the islands of the Sunda-range Sumatra-Java-Bali-Lombok-Sumbawa-Flores-Lomblen-Pantar and do not exist farther on to the east in Alor, Kambing, Wetter and Roma, but reappear still farther eastwards in the curving chain of volcanic islands Dammer-Teon-Nila-Serua-Manuk-Banda.

According to Verbeek [1]) the volcanoes of the Banda Sea form an ellipse separated from the volcanic Sunda islands by the "strip of older rocks", drawn by him across Wetter. In a paper on the recent mountain-building movements in this region [2]) we have designated the arch of volcanic islands in the Banda Sea, for the most part situated below the sea surface of the sea, as a continuation of the range of the Sunda islands. On this basis the non-existence of volcanoes in a certain portion of this chain must be accounted for as a phenomenon resulting from causes of a more general nature.

We enumerate, with reference to the volcanic phenomena, the following characteristics of the two curving rows of islands in the eastern part of the Indian archipelago.

a. The outer row (Timor-Tenimber-Ceram-Buru) is entirely devoid of volcanoes. These are to be found only in the inner row (Flores-Wetter-Dammer-Banda).

b. Occasionally the active volcanoes are also missing in the inner row, *just where the two rows approach each other most, i. e. to the North of Timor* (see Fig. 1).

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[1]) R. D. M. Verbeek. Molukkenverslag Jb. v. het Mijnwezen 1908 Wet. Ged. Kaart N⁰. 1.

[2]) H. A. Brouwer, Over de bergvormende bewegingen in het gebied der boog-vormige eilandenreeksen in het oostelijk deel van den O.-I. Archipel. Versl. Kon. Ak. v. Wet., Amst., Nov. 1916.
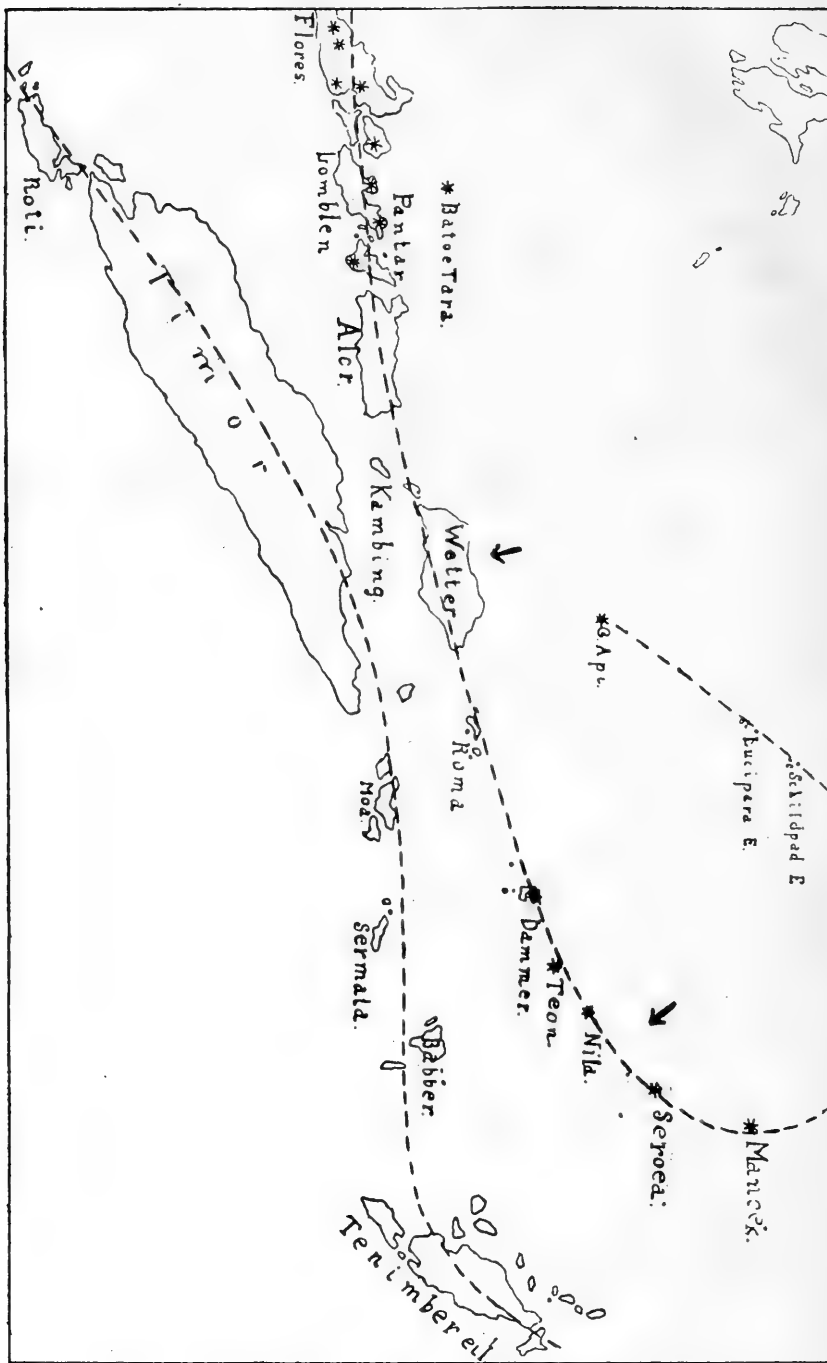
Fig. 1. Crustal movements and volcanic action in the South-eastern part of the East Indian Archipelago.

— ·· — — — the geanticlines.

* centra of recent volcanic action.

c. Where active volcanoes do not exist in the inner row, products of extinct volcanoes cover a vast area. They also occur in the outer row (North coast of Timor).

The island of Lomblen still contains numerous, partly active volcanoes; in the eastern part of Pantar six independent vents of eruption are known, only one of which (the Gg Api) still displays the action of the solfatara-stage; the Delaki still exhibits a beautiful cone-shape, but at present is wooded to the very top. In the east of Alor there is an ancient volcano, the Peak of Alor [1]), 1655 m. high and to the south of it we find a second, lower peak ; both have a cone-like shape, but through long erosion they have lost the beautiful regular appearance of a cone. Still farther towards the east we distinguish the old volcano of Pulu Kambing, north of Timor Dilli, farther again in Lirang and Wetter diabases, gabbros and granites have been laid bare by erosion over vast areas. Roma again consists entirely of volcanic products, tuffs, breccias, conglomerates and solid lava in dykes and flows [2]), however without active vents, which do not reappear again before Dammer, farther eastward.

It would seem then that, starting from Wetter, — where the two curving rows of islands are closest to each other — the volcanoes became extinct at a later period according as they were farther removed from Wetter. Lower down we shall discuss more fully *the relationship between the divergence of the rows of islands and a more prolonged volcanic action consequent on a progressing distance between the two rows.*

d. In those parts of the regions under consideration where no active volcanoes occur, elevated coralreefs have covered extensive areas. In Pantar coral limestone covers all the older volcanoes up to a certain height above the sealevel (in this island 400 m.); only the young volcanoes Delaki and Iljasi Awieng with the still active vent Gg Api are not covered with limestone at their bases.[3]) In Alor the elevated reefs seem to reach a height of 700 m. above the sealevel, they likewise overlie the products of the slightly coniform Peak of Alor. More towards the east in the volcanic island of Kambing (± 1000 m. high) the volcanic products are covered by terraces of coral limestone to a great height (± 700 m.) [4]). Little is known as yet about the occurrence of elevated reefs in Wetter and Roma; in Wetter they occur along the coasts up to 80 or 100 m.

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[1]) R. D. M. VERBEEK, l. c. p. 375.
[2]) Ibid, p. 435.
[3]) Ib., p. 15.
[4]) Ib., p. 376.

above the level of the sea and in Roma they [1] have reached con-
siderable heights. However, as far as the islands west of Wetter
are concerned, our assumption, that volcanic action lasted the longer
the more the islands were removed westwards from Wetter, is borne
out by the occurrence of elevated coral reefs.

e. Whether there has been a shifting of the volcanic action in
a direction perpendicular to the row of islands cannot be well
made out.

It might be supposed, that it has shifted inward, because to-day
volcanoes occur only in the inner row; but the present configura-
tions of the landsurface resulted from the recent crustal-movements
and the region north of the islands in fig. 1, is nowadays covered
by the sea. The volcanic action may, in the tertiary period, have
affected a broader tract, while at present it is confined to a narrower
strip comprising the inner row of islands.

Having recorded these characteristics, we will now discuss first
of all the origin and the shape of the two curving rows of islands.

Origin of the rows of islands.

In an earlier paper we have demonstrated [2] that the elevation of
the islands, encircled by deep ocean-basins, must be looked upon as
a result of renewed mountain-building forces and that these move-
ments, just as the tertiary, are apt to proceed towards the "Vorland".
Their intensity has been variable, nor was it equal for various
parts of one and the same row in a definite period, so that some
parts may rise higher than the other and locally also subsidence
may occur. We will confine ourselves to the region under consider-
ation. In Timor a period of intensive crustal movements, persisting
into the miocene, was succeeded by a prolonged denudation of the
landmasses emerging from the sea. A large part of the island has
afterwards been submerged again and a pliocene formation, whose
oldest deposits consist of pure Globigerina-limestone devoid of terri-
genous elements rests unconformably on the older formations, as
has been discussed in detail by MOLENGRAAFF [3] [4]). In plio-pleistocene

[1] Ib., p. 435.

[2] H. A. BROUWER, l. c.

[3] G. A. F. MOLENGRAAFF, Folded mountain chains, overthrust sheets and block-
faulted mountains in the East-Indian archipelago. C. R. XIIth congr. geol. intern.
Toronto 1913, p. 693

[4] Ibid. On recent crustal movements in the island of Timor and their bearing
on the geological history of the East-Indian Archipelago, Proc. Kon. Ak. v. Wet.,
29 June 1902.

time a great part of Timor was still covered by a sea full of coral-islands and reefs, from which the higher mountains emerged as islands, similarly to what may still be observed farther eastward in the islands, east of Moa. Ever since a general elevation above the sealevel has been going on, which may still be proceeding. Signs of this uprise can be witnessed in all the islands of the region under consideration.

The foregoing points to a decrease of tangential pressure after the miocene process of mountain building and to a renewed intensification of that process in the plio-pleistocene, which possibly still continues.

Shape of the rows of islands.

For a more comprehensive exposition we refer to the map, accompanying our paper on the orogenetical movements in the discussed region [1]) [2]); from fig. 1 it is, however, sufficiently evident that the outer row, in the part Rotti—Timor—Babber, has its concave side turned to the Australian continent, whereas the inner row is convex on that side. Again, the outer row exhibits outward bends in the Tenimber-islands and the Kei-islands, just where depressions occur in the "Vorland" (Australian Continent with Sahul bank and Arafura sea). The inner row does not bend in that way, the curve progresses regularly.

A comparison of the two curving rows of islands of the East-Indian archipelago will show, therefore, that *the outer row has better adapted itself to the shapes of the "Vorland" than the inner one.*

In the paper alluded to above we have compared the outward bends of the outer row in the Kei- and Tenimber-islands with the movement of the Pennine overthrust sheets of the Alps into the lower parts of the hercynian mountains against which they were forced upwards. The strong crustal movements in the miocene period have been rather weak in the Kei-islands; the eocene is not intensely folded in Groot-Kei, the miocene is not folded at all [3]), while farther west the strata seem to be more strongly folded, as in a new island near Ut (Klein Kei-group) contorted, approximately vertical strata probably of eocene-marl and limestone, were observed. This indicates that the prolongation of the intensely folded and overthrust mountain range of the Timor islands in the direction of Ceram, did not yet show the marked outward bend near the Kei islands, and was

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[1]) H. A. Brouwer, l. c. Fig. 1.

[2]) H. A. Brouwer. Ueber Gebirgsbildung und Vulkanismus in de Molukken. Geol. Rundschau VIII, 1917, p. 197.

[3]) R. D. M. Verbeek, l. c. p. 501.

nearly parallel with the present inner row with the young active volcanoes.

The characteristics of the rows of elevated islands and of the deep seabasins between them are indicative of a renewal of the mountain-building process which, in the miocene period has pushed the mesozoic and anterior tertiary sediments in the direction of the "Vorland." They are not contrary to the assumption, that these movements take place again in the direction of the Vorland. When these movements persist, the rising of the islands will be attended with a removal in that direction, as e.g. was the case with the Kei Islands ever since the miocene movements. The sea-basins will then get narrower and the initial phase of the future overthrust sheets manifests itself on the surface as anticlinal and synclinal undulations in the direction of the Vorland.

Relation of volcanism to crustal movements.

The relation between eruptive activity and violent movement in the earth's crust, with regard to time as well as place, is a matter of general knowledge; geologists only disagree as to the cause of either. Volcanic outbursts constitute only one type of eruptive pheno-mena that require penetration of the earth's crust by the magma.

In the case of folding movements the equilibrium will be restored by the coincidence of displacements in the crust with the movements of the molten magma.

With regard to the most recent crustal movements in the region under discussion, we assume that in the Moluccas they are connected with folding at a greater depth. If tangential pressure reveals itself in the formation of normal folds, the molten magma will, under compression from all sides, sometimes force its way through the crust with unequal strain, first of all near the tops of the anticlines, where tension takes place; active volcanoes may then appear on the top of the mountain chain (in our case the row of islands). The same holds good also for oblique folds, for the time the strata adhere to each other; it is evident, however, that for several reasons during the folding process the independent movement of the volcanic magma can be prevented, for example when fan-shaped folds are formed that blocked up a magma-reservoir.

In case of disruption the relations are different: the tension in the anticlininal and synclinal tops disappears or decreases and the vents of the volcanic magma leading to the surface, maintained by the tension, can gradually be stopped up.

Movements on a large scale will give rise to overthrust sheets, where one mass of rock has been pushed bodily over another; the earth's crust in situ will increase in thickness, an additional reason for the stopping up of the volcanic vent. A new way is opened for the magma to reach the surface along the thrust-planes; most often the magma, if it reaches the surface will appear on a lower level i.e. in the region here discussed below the surface of the sea along the outer margin of the row of islands and movements in the direction of the "Vorland" will cause the volcanic products to be gradually overlain by the moving masses.

Disruption of the strata may occur abruptly without any folding. It goes without saying that in this case there is no question about an exit for the magma on the tops of the anticlines; the disturbance of the equilibrium caused by the movements in the earth's crust are directly attended with an increase of thickness of the crust where the crustal movements take place. The above shows sufficiently that the magma can reach the surface while folding is in progress, but that the place where and the time when volcanic activity will appear, depend on the character of the crustal movements.

The magma can find an egress also without the aid of crustal movements. By assimilation of adjacent rocks or by magmatic stoping [1]) the magma can force its way upwards and extrude by de-roofing, as for instance DALY [2]) assumes for the rhyolite-plateau of the Yellowstone National Park, UssING [3]) for the Greenland intrusions and myself [4]) for the intrusion of the Pilandsberg in the Transvaal.

This volcanic activity may manifest itself particularly in the intermittent periods of rest of crustal movements. Secondly, the magma will only be able to penetrate through the crust in places where it is comparatively thin, because otherwise it will have cooled down too much and have lost much of its mobility. Consequently no effusion can be expected where the crustal movements have engendered a thickening of the earth's crust; this will then more likely be possible along the margins of the anticlines, particularly along the inner ones.

[1]) R. A. DALY, Igneous rocks and their origin, 1914, p. 194.

[2]) Ibid, p. 122.

[3]) N. V. UssING, Geology of the country around Julianehaab, Greenland, Medde lelser om Gronland. Vol. XXXVIII and Mus. de Min. et de Géol. de l'Université de Copenhague. Comm. Geol. N⁰. 2. 1911.

[4]) H. A. BROUWER, On the origin of primary parallel structure in lujaurites. Proc. K. A. v. W., 8 Nov. 1912.

Ibid. On the geology of the Alkalirocks in the Transvaal. Journ. of Geol. XXV, 1917, p. 768.

When testing the above hypothetical considerations to the recent crustal movements in the region discussed, it appears that during these movements in the outer row of islands the magma has not reached the surface on the top of the geanticline. It is possible, however, that also there tangential pressure has revealed itself — anyhow initially — by folding without any breaking of the strata. So far as the present geological data enable us to judge, the same applies to the island of Wetter, close to the outer row of islands.

The volcanic rocks occurring along the inner margin of the row of islands i.a. in the north of Dutch-Timor and in Ambon[1]), are anterior to these crustal movements and perhaps were evolved by the anterior folding, which culminated in the miocene period. In the inner row of islands older but also young-volcanic rocks are found to a vast extent.

Volcanic action continues into the present time, but seems to extinguish gradually after having been intensified most likely with the renewal of the crustal movements. The volcanic activity was more prolonged consequent on a progressing distance from the outer row of islands, and from the "Vorland".

It would seem legitimate to assume that the folding movements were of the character described first in those parts that were nearest to the "Vorland", whereby the connection of the magma with the surface was broken. We refer to the above mentioned more complete adaptation of the outer row of islands to the configuration of the Vorland. The same will be the case in the islands east and west of Wetter, of the inner row, if the folding forces and the accompanying movements persist in the direction of the "Vorland". We see in the inner row of islands of the South eastern Archipelago an instance of *extinction of volcanic activity on the top of the geanticline during a renewal of the mountain building process.*

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[1]) Ibid. Geol. verkenningen in de oostelijke Molukken. Feestbundel Prof. Dr. G. A. F. MOLENGRAAFF, Verh. Geol. Mijnb. Gen. 1916, p. 38.

Geology. — *"On the Age of the Igneous Rocks in the Moluccas"*.
By Prof. H. A. BROUWER. (Communicated by Prof. G. A. F.
MOLENGRAAFF).

(Communicated in the meeting of Jan. 27, 1917).

In VERBEEK's [1]) latest geological memoir on the Moluccas, eruptive
rocks have been classified as follows:

1. *old basic igneous rocks* mostly of pre-permian age (azoic and
palaeozoic). Some may possibly be mesozoic. Petrographically are
distinguished peridotite, serpentine, gabbro, diabase porphyrite with
their tuffs and breccias, diorite and diorite-porphyrite, the last two
of minor significance, etc.

2. *granitic rocks* probably all of pre-permian age.

3. *old-meso-volcanic igneous rocks*. Older melaphyres, quartz-
porphyries and quartz-porphyrites, probably also some diabases and
diabase porphyrites. VERBEEK points out that no conclusive evidence
has as yet been adduced to establish the age of the rocks classed
among this group; he also surmises that part of them still belongs
to the permian formation.

4. *young-meso-volcanic igneous rocks* (*cretaceous*), andesites, dacites
and acid melaphyres with bronzite. Perhaps they belong partly to
the old-meso-volcanic igneous rocks, another part may be even of
old-tertiary age.

5. *tertiary igneous rocks* nowhere seem to go back to the eocene,
because the nummulitic limestones are entirely devoid of debris of
andesites, with which miocene sediments abound.

a. leucite- and nepheline rocks (old miocene or younger) considered
to be the oldest group on account of the structure of the volcano
Lurus in Java with an older rim of leucite basalt and a younger
cone of hornblende-andesite.

b. old hornblende-andesites and biotite andesites with their tuffs
and breccias (miocene). They have an individual existence, rarely
do they constitute the base or the oldest rim of the large volcanoes
of which some are still active. The latter cannot be separated from

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[1]) R. D. M. VERBEEK. Molukken Verslag. Jaarb v. h. Mijnwezen 1908. Wetensch.
Ged. p. 737 seqq. (Rapport sur les Moluques).

the younger volcanic products and therefore they have been united with them.

c. old pyroxene-andesites and basalts with their breccias and tuffs (miocene). What has been said sub *b* also refers to them.

6. *young volcanic products*, chiefly of quaternary age, also pliocene and recent. They form the young volcanoes which have been formed from the young-tertiary through the quaternary period while some of them are still active.

The above goes to show that of many igneous rocks, that have been classed among a certain group, the age is difficult to establish. Recent investigations have yielded fresh data which prompted us to study again the age of the several igneous rocks.

Ad 1.

VERBEEK suggests the possibility that some of these rocks are mesozoic, without being able to adduce any evidence for his hypo- thesis. According to him only some places show distinctly the presence of pre-permian rocks, for example the island of Letti, where diabase- breccias are believed to be superposed with permian limestone with crinoids. Moreover the peridotite of Ambon, as is proved by the granite dykes, is older than the last-mentioned rocks, while the granites themselves are believed to be of permian age, as the sand- stone formation of Ambon, to which permian or anyhow young- palaeozoic age was assigned, consists of débris of granite.

We must contend that:

a. the argument for a pre-permian age in the island of Letti falls through, as the permian limestones occur as blocks only, which may have been brought to this place by overthrusts [1]).

b. It is not possible yet to determine the age of the sandstone formation of Ambon, by the fossils which have been found in the limestones, that occur in the formation [2]). However, the facies is very much like that of the upper-triassic-rocks of Ceram [3]), in the neighbourhood of Ambon and we believe it to be of the same age. Proofs of the pre-permian age of granites and peridotites are neither afforded by sandstones built up of the débris of granites. Failing any evidence for a pre-permian age we must draw attention to the

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[1]) G. A. F. MOLENGRAAFF and H. A. BROUWER. De geologie van het eiland Letti. Ned. Timor Exped. 1. Jaarboek v. h. Mijnwezen. 1914. Verh. Deel I. p. 28.

[2]) K. MARTIN in Tijdschr. Kon. Ned. Aardr. Gen. XVI. 1899. p. 656.

G. BOEHM. Ueber Brachiopoden aus einem älteren Kalkstein der Insel Ambon. Jaarb. v. h. Mijnwezen. 1905. Wet. Ged. p. 88. seqq.

[3]) H. A. BROUWER. Geol. Verkenningen in de oostelijke Molukken. Feestbundel Prof. G. A. F. MOLENGRAAFF. Verh. Geol. Mijnb. Gen. Geol. Serie III. 1915. p. 36.

fact that in the islands of the archipelago outside the region of the Moluccas such rocks as the "old basic igneous rocks" are of frequent occurrence, for instance in Celebes, Borneo, and Sumatra. For many of them in Sumatra only a pre-oecene age has been established; in Borneo several must be grouped as cretaceous, as has also been observed already by VERBEEK.

In the eastern peninsula of Celebes near the Moluccas HoTZ[1]) describes peridotites and volcanic breccias conformable between the lower neogene strata, and not far from it sheets of amphibole diorite have been observed by WANNER[2]) between the marls of the same age. In the environs of the Tukalu mountains peridotites and volcanic breccias occur conformably in the partly tertiary, perhaps partly mesozoic "Buru-formation", while, conversely, limestone with chert occurs also in the basic eruptive rocks.

Furthermore it may be added:

a. that in Timor in the permian and triassic sediments basic intrusive- and effusive-rocks and their tuffs are of frequent occurrence.[3])[4])

b. that in the valley of the Nimassi (Central Timor) intrusive sheets of diabase occur with distinct contact phenomena in upper-triassic limestone, as demonstrated by me during Prof. MOLENGRAAFF's Timor Expedition.

c. that along the coast of Dutch Timor basic and more acid eruptive rocks occur frequently together with serpentine and serpentine conglomerate, which may belong to the tertiary (or young mesozoic) period as deemed plausible by me elsewhere. [5])

d. that in the North-Western part of the island of Great-Obi andesite which is quite similar to the young andesites of the archipelago is overlain conformably by serpentine. [6])

e. that in the island of Letti are found partly intensely meta-morphosed basic effusive rocks of permian and probably also of later origin. [7])

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[1]) W. HoTZ. Vorläufige Mitteilung über geologische Beobachtungen in Ost-Celebes. Zeitschr. der Deutsch. Geol. Ges. 1913. Monatsber. n⁰. 6. p. 329.

[2]) J. WANNER. Beiträge zur Geologie des Ost-Arms der Insel Celebes. Neues Jahrb f. Min. etc. Beil. Bd. XXIX. 1910. p. 765.

[3]) J. WANNER Geol. von West-Timor. Geol. Rundsch. IV. 1913. p. 145.

[4]) G. A. F. MOLENGRAAFF. Folded mountain chains, overthrust sheets and block faulted mountains in the East Indian Archipelago. Compte Rendu du XIIme Congr. Geol. Intern. Toronto. 1913. p. 689 seqq.

[5]) H. A. BROUWER, l. c p. 38.

[6]) Ibid. p. 45.

[7]) G. A. F. MOLENGRAAFF and H. A. BROUWER. De geologie van het eiland Letti. l. c. p. 22 seqq.

From the foregoing we feel safe to conclude *that among the so-called old basic eruptive rocks of the Moluccas there are rocks of young palaeozoic, mesozoic and probably of tertiary age, and that nothing can be said for certain about the occurrence of rocks older than permian.*

Ad. 2.

It has been supposed that the granitic rocks of the Moluccas are of pre-permian age, because, anyhow in Ambon, a young palaeozoic sandstone-formation consists of débris of granite. As observed above, we could for this formation rather assume an upper triassic age and the sandstones may as well consist of the débris of crystalline schists, so that there is no proof for the supposed pre-permian age of granites in Ambon.

Elsewhere we reported [1]) that in the islands of the archipelago outside the Moluccas the occurrence of mesozoic granites has been proved or rendered highly plausible by the investigations of MOLEN-GRAAFF, SCRIVENOR (for Malacca), TOBLER, VOLZ and the present writer. To this we can add for Celebes the investigations of VAN WATER-SCHOOT VAN DER GRACHT [2]) and ABENDANON [3]), which even lend support to the supposition that tertiary granitic to dioritic rocks occur in this island. For the Moluccas we refer to the following facts:

a. that granitic to dioritic and gabbro-like to peridotitic rocks sometimes occur in close alliance. Even where dykes of granite occur in peridotites, the granitic rocks can in some places be little younger than the peridotites and may have originated by differentiation from the same mother magma.

b. Investigations in the Sulu-islands by WICHMANN [4]) and myself [5]) point to the occurrence of post-jurassic granitic rocks in connection with contact-phenomena which have been observed in rocks of jurassic appearance.

Again the above warrants the conclusion *that no positive evidence has as yet been brought forward supporting the occurrence of pre-permian granitic rocks, whereas it has positively been proved that*

[1]) H. A. BROUWER. On the post-carboniferous age of granites of the highlands of Padang. Proceed. Kon. Ak. v. Wet. Amst. XVIII. 1915. p. 1513 seqq.

[2]) W. A. J M. VAN WATERSCHOOT VAN DER GRACHT. Voorloopige mededeeling in zake de Geologie van Centr.-Celebes. Tijdschr. Kon. Ned. Aardr. Gen XXXII. 1915. p. 118 seqq. en Jaarb. v. h. Mijnwezen. 1914. Vol. II.

[3]) E. C. ABENDANON. Geologische en Geographische doorkruisingen van Midden-Celebes. Deel I. Leiden 1915. p. 58.

[4]) A. WICHMANN. Over gesteenten van het eiland Taliaboe. Versl. Kon. Ak. v. Wet. Amst. Juni 1914.

[5]) H. A. BROUWER Geologische Verkenningen enz., l. c. p. 43.

younger, even tertiary granites are recognised in the Moluccas or in the neighbouring regions.

Ad 3.

Only few rocks are included by VERBEEK among his group of old-meso-volcanic igneous rocks. He deems it possible that part of it still belongs to the permian formation, while he emphasizes the impossibility of settling the age-question.

As regards the melaphyres of Timor, some of these rocks we consider to be of permian age, to which view also VERBEEK inclines [1]), and which has also been established by our as yet unpublished investigations of the Timor-Expedition led by Prof. MOLENGRAAFF.

These investigations also established the occurrence of similar old mesozoic rocks, while it is possible that a large part of the so-called "old-mesozoic eruptive rocks" is of much later young-mesozoic or tertiary age. To the latter belong for instance the melaphyres with hyaline crust, quartz-porphyries and dacites of Timor's north coast; besides the latter rocks also serpentines, serpentine breccias, serpentine conglomerates and tuffs occur.

In our judgment, therefore, not only among the so-called "old-basic-igneous rocks", but also *among the so-called "old-meso-volcanic-igneous of the Moluccas rocks occur of young palaeozoic, mesozoic and probably also of tertiary age.*

Ad 4.

Likewise the age of the young-meso-volcanic igneous rocks of cretaceous (?) age has, according to VERBEEK, not yet been ascertained. Part of them he is inclined to include under his old-meso-volcanic igneous rocks, others may even be old-tertiary. This group comprises only andesites, dacites and acid melaphyres with bronzite of Ambon, further andesites and dacites of the neighbouring islands of Haruku, Saparua and Nusalaut and of Western-Ceram, and finally horn-blendepyroxeneandesites of Amblau and pyroxeneandesites with vitreous crust of Wetter. Their being grouped together is due on the one hand to their fresh appearance, whereby they distinguish themselves from older rocks, while on the other hand they are different from the East-Indian tertiary igneous rocks.

In another paper [2]) we have described in detail that the points of distinction from other tertiary igneous rocks are immaterial to the establishment of the age. So, for instance, the enclosures of garnet

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[1]) R. D. M. VERBEEK. l. c. p. 359.
[2]) H. A. BROUWER. Geologische Verkenningen. l. c. p. 34 seqq.

and cordierite, recognised in rocks of Ambon, originate from the substratum, while the considerable amount of bronzite typefies the ambonites, it is true, so that they are designated by a separate name, but this does not necessarily point to a difference in age.

In discussing the "old-meso-volcanic igneous rocks" we have already observed that a great number of the rocks of this group may very well be looked upon as a much younger, young-mesozoic or tertiary formation. We alluded first of all to the melaphyres, some with a vitreous crust, of Ambon, Kelang, Wetter and Timor's northcoast and the quartz-porphyries and dacites of the same coast. Whereas VERBEEK does not separate the melaphyres of Timor and asserts this to be a reason for surmising that melaphyres of various ages occur in the eastern archipelago, and that, for example, in Ambon the melaphyres can be divided into two groups, I on the other hand feel inclined to class together the rocks of Ambon and to separate in Timor an older group (among which the permian melaphyres) from a younger (among which the rocks with the vitreous crust of the northcoast).

The melaphyres with a vitreous crust of Timor's north coast, namely, are of a totally different character and appear under totally different conditions, from the permian melaphyre-like rocks of the island. The former are limited to the north coast and united as one whole with other basic and also with more acid rocks (quartz-porphyries, dacites) presenting a great similarity to the known Ambon rocks. A typical feature for instance is the occurrence of melaphyres with vitreous crust, common to the rocks of either island. The glassy Java melaphyre, which VERBEEK invariably called cretaceous[1]), but now considers to be older with reference to the data from Timor, can, on this basis, be comprised again among the cretaceous system, and the rocks of Timor's north coast, Wetter, Ambon and South-West-Ceram can for the present be all assigned to the tertiary or young-mesozoic rocks. To this it may be added that MARTIN[2]) adopts a probable tertiary age for the rocks in Ambon.

When summarising the above we arrive at the following conclusions:

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[1]) R. D. M. VERBEEK and R. FENNEMA. Geologische Beschrijving van Java en Madoera, Amsterdam 1896.

[2]) K. MARTIN. Einige Worte über den Wawani, sowie über Spaltenbildungen und Strandverschiebungen in den Molukken. Tijdschr. Kon. Ned. Aardr. Gen. XVI. 1899. p. 709 seqq.

Ibid. Reisen in den Molukken. Geol. Teil. Leiden. 1903. Nachträge.

a. the available data do not justify us in separating a group of older melaphyres from the so-called ambonites;

b. there is no reason for classing as a separate group the ambonites which present some typical characteristics, as regards their age.

c. together with the rocks with a vitreous crust of Timor and the accompanying rocks they should be included under one group of the same probably tertiary or young-mesozoic age, assumed by VERBEEK [1]) for some of these rocks.

We conclude, then, that the so-called "young-meso-volcanic igneous rocks" *are also considered by us to be of tertiary or young-mesozoic age,* but most likely the number of rocks to be brought together under this group may be much larger.

It may also be stated that andesitic to basaltic and augitic rocks of islands of the Misool-archipelago are held by WANNER [2]) to belong to the cretaceous system.

Ad 5.

It has been suggested of the tertiary igneous rocks that their age in the Moluccas and in Celebes nowhere goes back to the eocene, since the nummulitic limestones are entirely devoid of debris of andesites, which on the contrary occurs abundantly in the miocene rocks.

In the following pages we will comprise the Southern part of Central Celebes, because recent investigations have furnished us with important data concerning the age of tertiary igneous rocks.

That the leucite- and nepheline rocks are not the oldest tertiary igneous rocks, as VERBEEK [3]) presumed, because the volcano Lurus in Besuki (Java) consists of an older rim of leucite-basalt with a younger cone of hornblende-andesite, appears from the following considerations:

a. Close to the east of the Gg Lurus, leucite-free rocks are found [4]) side by side with leucite-bearing rocks in the old craterwall of the Gg Ringgit composed of leucite rocks. These leucite-free rocks (olivine- and basalts rich in iron ore, olivine-poor basalts or olivine-bearing augite-andesites and amphibole-augite-andesites) must therefore be older than a great part of the leucite rocks.

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[1]) R. D. M. VERBEEK. Molukken Verslag. l. c. p. 360.

[2]) J. WANNER. Beitr. zur Geol. Kenntniss der Insel Misol. Tijdschr. Kon. Ned. Aardr. Gen. XXVII. 1910. p 194.

[3]) R. D. M. VERBEEK. Molukken Verslag. l. c. p. 757.

[4]) H. A. BROUWER. Ueber leucitreiche bis leucitfreie Gesteine vom Gg. Beser (Ost Java) Central Blatt f. Min. etc. 1914. p. 1.

b. In the thick tuff-formation along the Saädangriver (South part of Central Celebes) may be distinguished according to ABENDANON[1]):

trachyte- and andesite-tuffs,

basalt- and leucitetephrite tuffs, leucite-basalt, leucitite and leucite-tephrite breccias,

trachyte-, andesite-, and liparitetuffs.

ABENDANON[2]) takes this tuff formation to be of old-eocene age i.e. younger than the old-eocene sandstone- and shale series of Pasar Kira and older than the lutetien-limestone. It is not certain though, whether this formation, as a whole, is posterior to the sandstone- and shale-series; maybe there are also. pre-tertiary rocks among them. VAN WATERSCHOOT VAN DER GRACHT[3]) reports that the eruptions in the West seem to have been anterior to those in the East and that the age of the volcanic series varies from the lower, anyhow the middle eocene to probably the miocene. The lowermost banks are still eocene as proved by nummulites occurring by the side of globigerines in the matrix and inclusions.

In the district east of the Latimodjong mountain range, where numerous varieties of andesites and mostly silicified andesitic tuffs occur, the oldest eruptions are deemed to be pre-tertiary, while the youngest seem to have stopped before the neogene. Beside eruptions of andesite others of liparite, trachyte, and dacite also occur[4]).

As to the age of the igneous rocks of South Celebes opinions differed very much up to very recently. VON STEIGER[5]) gave us a general view of the various opinions, to which we shall refer the reader.

That also here in the eocene, and perhaps prior to it, eruptions took place, is borne out by the occurrence of a silicified plagioclase-orthoclase tuff at the bottom of the limestone formation of the coal-field Tondong KURAH[6]) and by the andesite tuffs below the limestone near Kantisang, as described by BÜCKING[7]). The majority of the

[1]) E. C. ABENDANON. Celebes in of uit de Tethys? Tijdschr. Kon. Ned. Aardr. Gen. 1915. p. 358 seqq.

[2]) Ib. Geologische en Geographische enz. l. c. p. 222.

[3]) W. A. J. M. VAN W. V. D. GR. l. c.

[4]) E. C. ABENDANON. Geologische etc. l. c. p. 59, 60.

[5]) H. VON, STEIGER. Petrographische beschrijving van eenige gesteenten uit de onderafdeeling Pangkadjene en het landschap Tanette van het gouvernement Celebes en onderhoorigheden. Jaarb. v. h. Mijnw. 1913. pag. 171 seqq.

[6]) Id. p. 217.

[7]) H. BÜCKING. Beiträge zur Geologie von Celebes. Samml. des Geol. Reichsmus. in Leiden VII. Heft 1. pag 124.

eruptions, however, is younger, according to a record of 'T Hoen, who examined the coalfields of South Celebes. According to him, probably a short time before the deposition of the tertiary limestones had completely terminated, eruptions began all along the western side of South Celebes, which gave rise to the high western mountains; for the greater part they consist of tuffs, breccias and volcanic conglomerates of andesites, basalts and also. of leucite-rocks. The fragment of leucitite, mentioned by von Steiger [1]), as originating from a tuff between the coal-layers I and II of Bonto, appears on closer examination to belong to a weathered eruptive rock, as established by the engineer 'T Hoen. Considering that several weathered intrusive rocks occur in the neighbourhood, it is rendered highly plausible that the rock, from which the fragment of leucitite originates is also of an intrusive character; similarly the biotite leucite basalt found by Bücking [2]) near Kantisang overlain by old-tertiary limestone may also be an intrusive sheet. If so it would disprove the hypothesis of an eocene age of leucite rocks in South-Celebes.

Prof. Iddings, who travelled over this district in 1913, reports that numerous intrusive rocks occur, as dykes, intrusive sheets and perhaps as laccolites and as batholites, in the above-mentioned volcanic series and also in the tertiary sandstones with coal-measures and limestones. He mentions among others coarse grained shonkinites and essexites. These, then, are still younger than the volcanic series, which for the greater part is believed to be younger than the limestones. As known, the limestones of this district are assigned partly to the eocene and partly to the miocene period [3]).

In addition we refer to Hotz [4]) who assumes tertiary (to miocene) age for most of the basic eruptive rocks in the eastern peninsula of Celebes.

Available data, in some degree contradictory, seem to point out that the violent eruptions in South-Central-Celebes may have begun prior to the outbursts in South-Celebes; however, they may have been contemporaneous for a considerable time, especially if the volcanic formation in the former region goes back into the miocene, as is deemed probable by Van Waterschoot van der Gracht. Anyhow a considerable number of the tertiary igneous rocks in Celebes must be of eocene age.

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[1]) H. von Steiger. l. c. p. 124.

[2]) H. Bücking. l. c. p. 000.

[3]) R. D. M. Verbeek. Molukken Verslag 1 c. p. 55 seqq.

[4]) W. Hotz. Vorläufige Mitteilung über geologische Beobachtungen in Celebes. Zeitschr. d. deutsch. geol. Ges. Monatsb. 1913 Bd. 65. p. 333.

In this connection it must be kept in view that MARTIN [1]) adopts eocene age for a portion of the andesite breccias and the andesite tuffs in Java (étage m_1 of VERBEEK) and it is not out of the bounds of probability that similar rocks more to the east in the Sunda row of islands and elsewhere are likewise of old-tertiary age.

We have already pointed to the occurrence of numerous tertiary igneous rocks also in the eastern part of the Archipelago, when discussing the previous groups. When we dwelt on the rocks of Timor's north coast we abstained from mentioning that WANNER [2]) inclines to adopt a young-miocene age for the augite- and hypersthene-andesites and the andesite-tuffs in West-Timor between the rivers N. Bonat and Kapsali.

According to VERBEEK the tertiary igneous rocks are independent mountain ridges or cone-shaped hills; the bases of the old, crater-rims of the large, in part still active volcanoes, often made up of pyroxene-andesite and basalt, are probably somewhat younger (pliocene); they cannot, however, be separated from the younger volcanic products and will, therefore be treated together with the young volcanic products.

Ad 6.

The young-volcanic products (pyroxene-andesites to basalts) build up the volcanic massifs, which are often more or less coniform in consequence of the materials being ejected on all sides round the vent of eruption. They were built up from the young-tertiary period through the quaternary into the present time.

From the above considerations, to which others could be added, it is sufficiently evident that the results of recent investigations necessitate a revisal of VERBEEK's Memoir published in 1908, as the writer himself has anticipated repeatedly. Whereas he confines almost exclusively the intrusive rocks to his two oldest groups, it has been proved conclusively that basic and acid intrusive rocks occur in totally different geological series, while volcanic eruptions took place down from the young-palaeozoic, through the mesozoic and the tertiary up to the present period. They were extremely violent in the first and partly also in the second period, but seem to have been restricted chiefly to the region now occupied by Timor and

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[1]) K. MARTIN. Vorläufiger Bericht über geologische Forschungen auf Java II. Samml. des geol. Reichsmus. in Leiden. Bd. IX. p. 194.

[2]) J. WANNER. Geologie von West-Timor. Geol. Rundsch. Bd. IV. 1913. p. 146.

the adjacent islands. Very likely in young-mesozoic time a new period began of markedly violent igneous activity, which culminated in the tertiary and persists even in our days. Traces of this new period are scattered over a considerable part of the eastern archipelago.

When subdividing the eruptive rocks of the Moluccas according to their relative age into the following groups:

a young-palaeozoic to old-mesozoic igneous rocks

b young-mesozoic to tertiary igneous rocks

c young-volcanic products,

we are in a position to distribute a large number of the known eruptive rocks with complete certainty among one of these groups; for many rocks the subdivision might be carried down still farther. In every group the rocks might be subdivided again according to their petrographic characteristics. Some rocks, however, there are that may be older than young palaeozoic, while a large number are still known as boulders. Too little is known of them to establish their ages. In this connection we can subdivide the eruptive rocks first of all according to their petrographic characteristics. However, here again we meet with the difficulty that of a great many rocks no or, at all events, no detailed descriptions are at our disposal, so that we are not competent to judge of their structure and their mineralogical properties; moreover we are entirely or partially ignorant of the geological occurrence of many of them. For a classification from a chemical point of view we are absolutely destitute of sufficient information.

We distinguish the subjoined groups:

a. granitic to dioritic rocks

b. gabbro-like to peridotitic rocks (with part of the serpentines and diabases)

c. foyaitic to theralitic rocks

d. rhyolites and quartz-porphyries, trachytes and porphyries without quartz, andesites and porphyrites with keratophyres, alkalirhyolites, alkalitrachytes, trachyandesites

e. basalts, melaphyres, pikrites etc. (with part of the serpentines and diabases).

f phonolites, leucite- and nepheline-rocks, trachydolorites, tephrites and basanites, melilitebasalts, limburgites and augitites.

To each group should be added that part of the graniteporphyric and fine-grained equivalents and of the aplitic, lamprophyric and pegmatitic rocks, which corresponds most with it on the ground of the available data.

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For every separate group we will communicate what is known concerning the geological age:

Group a. The composition of the sandstone formation of Ambon composed of débris of granite, may indicate, but does not prove the occurrence of granites, which are older than upper triassic. Besides these we recognize numerous younger, post-jurassic and tertiary granitic and dioritic rocks in the Moluccas, in Celebes and also in the other islands of the archipelago.

Group b. Of this group rocks of young-palaeozoic, mesozoic, and tertiary age are known.

Group c. These rocks are known from Timor[1])[2]), but no reliable evidence of their age has been brought forward. In South Celebes there are shonkinites and essexites intrusive in the tertiary volcanic series of this region, from which a tertiary age can be deduced for these rocks.

Group d. Many of the rocks belonging to this group in the Moluccas and in Celebes are of tertiary age, may perhaps go back to a mesozoic age, while the basic representatives of this group among the basic eruptive rocks are numerous in the permian and old-mesozoic sediment series of Timor and adjacent islands. Among the younger volcanic rocks there are many andesites (in Celebes also acid effusiva). They are often hard to distinguish from the basalts, the two species of rocks being united by numerous transitions.

Group e. Are numerous in the permian and old mesozoic sediment series of Timor and adjacent islands; a great part belongs to the tertiary eruptive rocks mentioned sub *d*, a considerable portion of which may perhaps be traced back to the mesozoic. Basalts also are very numerous among the young-volcanic products.

Group f. We know leucite-bearing rocks of Sumbawa. They seem to be of young-tertiary age[3]), while even leucite-basanite has been recorded as a lavaflow on the Southern slope of the Tambora[4]). In Celebes leucite- and nepheline-bearing rocks are abundant. We have already observed that in South Celebes and in Southern Central

[1]) A. WICHMANN. Gesteine von Timor. Samml. Geol. Reichsmus. in Leiden. Serie I. 2. p. 85.

[2]) H. A. BROUWER. Neue Funde von Gesteinen der Alkalireihe auf Timor. Central Bl. für Min. etc. 1913. p. 570 seqq.

[3]) J. ELBERT. Die Sunda Expedition. Bd. II. Frankfurt a. M. 1912.

Cf. also G. RACK. Petrographische Untersuchungen an Ergussgesteinen von Sumbawa und Flores. Neues Jahrb. für Min. etc. Beil. Band 34. 1912. p. 42 seqq.

[4]) J. J. PANNEKOEK VAN RHEDEN. Voorloopige mededeelingen over de geologie van Soembawa. Jaarb. v. h. Mijnw. 1913. p. 20.

Celebes they are of tertiary, in part of young tertiary age. According to WANNER [1]) an augitite-like rock in the island of Bamdie of the Misool archipelago, seems to be of cretaceous age.

In Timor and Rotti camptonitic rocks occur, which probably are of permian age [2]).

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[1]) J. WANNER. Beiträge etc. loc. cit. p. 494.

[2]) H. A. BROUWER. Neue Funde. loc. cit. p. 576.

Ib. Voorloopig Overzicht der geologie van het eiland Rotti. Tijdschr. Kon. Ned. Aardr. Gen. XXXI. 1914. p. 613.

Geology. — *"On Reefcaps"*. By Prof. H. A. BROUWER. (Communicated by Prof. G. A. F. MOLENGRAAFF).

(Communicated in the meeting of November 30, 1918).

Proof of an uplift of the land relatively to the level of the sea can, in tropical regions, often be supplied by the presence of upheaved fringing reefs. Thus it will be seen that in the eastern part of the Indian Archipelago, where an elevation of the row of islands has taken place on a large scale ever since the plio-pleistocene period, upheaved fringing reefs, often forming continuous reefcaps occur in most of the islands, sometimes to a height of about 1300 m.

The character of the latest movements in the curving row of islands of the south-eastern archipelago, which resulted in[1]) the formation of these islands, has been discussed in an earlier paper[2]).

The latest mountain building is considered to be a revival of the intensive young-tertiary movements, the typical features of the islands indicating that, just as in the case of the tertiary, also with the youngest mountain building the movements are in the direction of the "Vorland" whereas near the surface mostly faulting is observed. The upheaval of the islands has not been simultaneous, nor equally intense in all places, while periods of temporary subsidence have probably interrupted the general elevation since the plio-pleistocene period. In this paper we shall try to ascertain whether there is any relation between the widely varying characters of the reefcaps we observed, and the character of the crustal movements. In this endeavour the aspect of the movement of the geanticlines during long periods will be brought to the front more than has been done heretofore.

The reefs at the time of their growth.

The growth of fringing reefs along parts of the coastline may be prevented by various causes, e.g. the lack of a solid substratum,

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[1]) G. A. F. MOLENGRAAFF. On recent crustal movements in the island of Timor and their bearing on the geological history of the East-Indian Archipelago. Proc. Kon. Ak. v. Wet. June 29, 1912.

[2]) H. A. BROUWER. Over de bergvormende bewegingen in het gebied der boogvormige eilandenreeksen van het oostelijk gedeelte van den O. I. Archipel. Versl. Kon. Ak. v. Wet. XXV, p. 768.

impurity of the water, and volcanic eruptions. If, however, reefs do develop, the shape of the living reefs depends largely on the stage of development of the crustal movements at that moment. In our discussion we assume a stable sealevel, because our conclusions will also hold for a moving sealevel. If the coastline remains stable for a considerable time or undergoes only slightly horizontal displacements, horizontal and thick reefs may possibly be formed; slightly vertical movements will perhaps increase especially the thickness of the reef, if the movement is a positive one, while negative movements will soon cause the reef to rise above the sea, even though its thickness and extent be only slight yet.

All these phenomena may appear simultaneously at points of the geanticline remote from each other, so that already while the material is forming which is to help in the composition of the reefcaps, considerable difference in the shape may occur.

The development of reefcaps.

After the reef has risen above the sea, the morphological changes, which were the combined result of the character of the crustal movements and the growth of the corals, are at an end. During the continued movements the reefs move along curves, whose shapes vary and are determined by the character of the crustal movements. These movements may again be alternately vertical or horizontal and downward, each type manifesting itself during a longer or shorter period. The shape of the curves is determined by the evolution of the geanticline on which the reefs were formed. The reefcap observed by us is the final product of these continual and varying movements. The reefs formed at a certain epoch on the surface of the sea, which, initially, were all lying in the same horizontal level, are, in a later stage of development, located in a plane of irregular shape. The oldest parts of the reefcap have undergone this change longer than the other portions.

Besides by the character of the crustal movements the form of these reefcaps is to a great extent also determined by erosion.

Influence of erosion.

In rising areas subject to strong erosion, it is no matter of surprise to find that of the portion of a reefcap that has for a long time been elevated above the sea-level, only some remainders are left, whereas the younger portions still present an unbroken cap. This will sometimes happen, but it is not the rule. There are namely

other factors besides time, which govern the influence of erosion on the reefcap, e.g. the nature of the substratum on which the reefs have been deposited and the power of resistance of the reefs themselves. If the substratum consists of soft rocks, which bring about landslips, while deep valleys are cut in the formations, as is the case with a great part of the mesozoic deposits in a number of islands of the eastern Indian archipelago, the uplifted reef over-lying it will soon crumble away.

If the reef is merely a thin crust covering the underground, it will disappear the sooner; thick reefs will resist erosion for a con-siderable time, and will occasionally act as a protective cover over a soft underground.

As already observed, thick reefs will form in places, where the coastline maintains itself for a considerable time, or has undergone only more or less horizontal or downward movements. As such they will afterwards constitute parts of the reefcap, whereas in those places where the coastline has long been exposed to strong negative movements only a thin reef can be evolved, which later on will occur as a thin part in the reefcap. This part is liable to disappear through erosion. For it is just with these strong negative movements that erosion often acts very forcibly, so that both factors co-operate to remove the effects of these movements from the reefcap. With short negative movements this will be manifested only in a terraced structure.

It will, therefore, frequently be seen that, at great heights above the sea-level, the reefcap is fully developed, whereas lower down towards the coasts it has totally disappeared or has been preserved only in detached fragments, while on the coasts themselves living corals are thriving well. Here we are reminded of our investigations in various localities along the north coast of the island of Rotti, along the coasts of Sermata, Great-Obi, Ceram and Timor, where the lower elevated reefs (if still any have been left) are for the greater part removed by erosion, e.g. if they have been preserved only on the ridges between the valleys, draining towards the coast. Along the North coast of Timor the thick reef of the Talau basin abruptly terminates near Balibo at a height of $\pm$ 610 m.[1]), between Balibo and the actual coast no trace of elevated coral reefs is found, whereas at the coast living corals are abundant. Here the reef may have been removed by erosion, in which process the above-mentioned conditions of a rapid erosion must have been present, while the

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[1]) G. A. F. MOLENGRAAFF, loc. cit., p. 128.

more elevated thick reef has been preserved, though it had been longer exposed to the eroding forces. If at a higher level a reef-cap is lacking, it is impossible to detect whether also here erosion has been at play, or whether this area has been uplifted from the sea ever since the beginning of the crustal movements.

It follows, then, that the influence of erosion upon the form of the reefcap can be estimated only for the tract beneath the highest reefs, which have been left intact by erosion.

Influence of faults.

The influence of faults on the form of reefcaps is, on the whole, confined to the dislocation of connected parts, which are brought in various positions at different levels. Faults having played a prominent part in the youngest crustal movements in the eastern archipelago, the form of the reefcaps may be supposed to have been largely affected by them. VERBEEK [1] e.g. assumes a fault across the peninsula of Huamual in Southwest Ceram, where the terraces of coral limestone appear south of Luhu to the height of 350 m. above sea level, while the lime more to the north scarcely reaches 100 m. In the continuation of this fault we find Hatusua (the eastern side Piru-bay), Paulohi and Tehoro (on Taluti-bay), which were afflicted more violently than other places by the earth- and seaquake of 30 September 1899, and also the steep south-eastern coast of Buru.

When faulting takes place in the neighbourhood of the coasts, downward as well as upward movements may be observed at short intervals and the growth of the living corals may exert its influence upon the shape of the forming reefcaps longer than usual.

The inclination of the geanticlinal axes.

In discussing the growth of the reefcaps it has been stated that every point of a forming reef will move along curves of various shapes. The horizontal component of the rate of movement, at a given moment is the resultant of two directions which are at right angles to each other, one of which coincides with the geanticlinal axis.

The vertical component determines the rising of the row of islands. The difference in the rate and the direction of the movements at different points gives rise to the morphological changes of the surface of the geanticlines of which we shall first consider those along the geanticlinal axis.

[1] R. D. M. VERBEEK. Molukken Verslag. Jaarb. v. h. Mijnwezen. Wet. Ged. 1908, blz. 550. FRENCH: Rapport sur les Moluques.

In virtue of the changes which this axis undergoes in a certain space of time, the inclination may increase in some places, decrease in others. If we suppose the top of the geanticline to remain in the same place, the different points of the axis will, at an increase of inclination, perform movements on either side, which are horizontal towards the top and vertical in a downward direction. Also with a slight rise of the top, downward as well as horizontal movements may occur at a lower level along the axis. In this case it will, at a certain stage of the evolution of the geanticlinal axis, depend on the height of the sealevel, whether a reef formed at this time will be moved up or down. The displacement of the reef will invariably be also in a horizontal direction, fault-movements are left out of consideration here. Conversely the transverse coasts may rise, while the top of the geanticline is descending at a certain height of the sealevel.

Generally the top will not remain in the same place, but will be moved both in horizontal and in vertical direction; moreover the inclination on either side of the top will not decrease or increase in the same way. It does not follow that during these irregular movements the transverse coasts will exhibit a similar behaviour, and generally speaking it may be said that, if the distance from the top of the geanticlinal axis to the coastline, i.e. in the case of the larger islands, be sufficiently great, the vertical component of the direction of the movement at the tops need not be similarly directed to that at the points of intersections of the geanticlinal axis and the sealevel. This vertical component varies at various points along the axis.

The inclined geanticlinal axes in the present-day stage of mountain building e.g. are easily distinguishable in the islands of the Timor group separated by straits, and from the above it may be inferred first of all that the rate of movement latterly observed on the transverse coasts of the larger islands, is not necessarily equal to the rate of movement of the tops, nor need it be of the same direction. This also holds for the earlier stages of the mountain building process. Secondly it appears, therefore, that the height to which a reef has been upheaved, by no means depends only on the time elapsed since its formation, but on the evolution of the geanticlinal axis so that reefs of the same age may be elevated to different heights[1]) and the highest reefs may sometimes not be the oldest.

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[1]) As e.g. in Timor. Cf. G. A. F. MOLENGRAAFF, l. c., p. 132 and J. WANNER, Geologie van West-Timor. Geol. Rundschau IV, 1913, p. 139.

Asymmetrical Reefcaps.

An asymmetrical development of the geanticlinal axis on either side of the highest points yields asymmetrical reefcaps. This asymmetry is brought about by the variable degree and direction of the horizontal component of the rate of movement.

We purpose to consider this development more particularly in a plane at a right angle with the geanticlinal axis, an instance of which is found in the island of Rotti and the island of Jamdena of the Tenimbergroup. Here the reefcaps rise from the northwestern coast gradually up to the main watersheds of the islands, thence descending rapidly towards the south-eastern coasts. Parts of the reefcaps have disappeared through erosion.

The relationship of these asymmetrical reefcaps, to certain crustal movements may be seen from the coincidence of the asymmetrical structure with marked outward bends of the row of islands, to which the named islands belong [1]).

The island of Jamdena lies nearly opposite to a depression in the Sahul-bank and Arafura sea; here the geanticlinal axis met with less resistance and consequently could be moved more easily than elsewhere in the direction of the "Vorland". The horizontal component of the rate of movement at a right angle with the geanticlinal axis may be considerably larger than the vertical; in connection with this the uprise above the sea will be less, while the unequal size of the horizontal components for various points may increase the asymmetrical forms during the development or decrease them locally. Furthermore it follows that what has been said about the development of the geanticlinal axes for the transverse coast is also applicable to the movements along the longitudinal coasts and also to the relative age of reefs, raised to different heights. The asymmetrical reefcaps to whose development the horizontal movements have been highly instrumental, will rise less high above the sea than the symmetrical, supposing the mountain building forces to be equal. In this connection we may compare the reefs of the island of Timor,
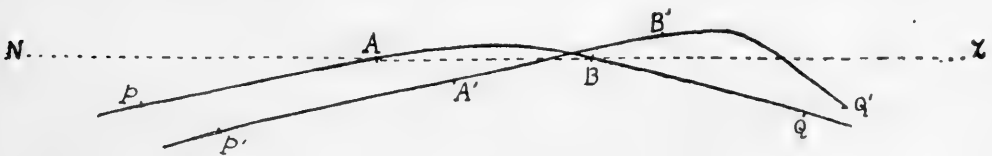

Fig. 1.

[1]) H. A. BROUWER, l. c., p. 770—772.

upheaved to about 1300 m., with those of the islands of Rotti and Jamdena elevated respectively to ± 470 and ± 150 m, which may be of the same geological age.

Downward moving longitudinal coasts sometimes occur with rising islands. Let us take e. g. one of the possible cases in the development of an asymmetrical reefcap, as is shown in Fig. 1. The points P, A and Q will, in a later stage of development have reached P_1, A_1 and Q_1. The sealevel is indicated by the line NZ. The portion AB of the geanticline rose above the sea in the initial stage as an island, and may possibly have been covered by a continuous reefcap.

During the development into the second stage, discussed by us, the island will increase in circumference and rise higher above the sea. On the north coast, however, downward movements are observed, while the South coast is moving upwards.

What was originally the oldest reefcap, AB, will have been transformed and partly disappeared under the sea, while the highest reefs in the second stage are by no means the oldest, so that older reefs will occur on a lower level than the younger ones.

In connection with the above-mentioned downward movement along the gently sloping part of the asymmetrical geanticline, we refer to the drowned river valleys, observed by us far inland along the northwest coast of the island of Jamdena of the Tenimber group. The downward slope can be only apparent also here, relative to a postglacial rise of the sealevel [1] [2].

In contradistinction to Timor, Rotti and Jamdena are now also in their central parts covered for the most part with a continuous reefcap. We attribute this to the influence of erosion in connection with the predominating horizontal movements at right angles with the geanticlinal axis. Along the longitudinal coasts of the last-mentioned islands these movements caused more resistant reefcaps to be formed, which moreover were not upraised so high, so that for two reasons the reefcap was attacked less while it disappeared completely (or for the greater part) along the rapidly raised longitudinal coasts of central Timor also for two reasons.

Of the aspect of asymmetrical reefshields it is often said that one coast is lifted more than the one opposite. This assertion, however, does not assign significance enough to the horizontal component of

[1] R. A. DALY. The glacial-contral theory of coral reefs. Proc. Amer. Acad. of Arts and Sciences. Vol. 51. N⁰. 4, p. 157. 1915

[2] G. A. F. MOLENGRAAFF. The coral reef problem and Isostacy. Proc. Kon. Ak. v. Wet. XIX, N⁰. 4.

the rate of movement and the continual morphological change of the geanticline, which have often been so influential in the development of the reefcaps. In the case illustrated in Fig. 1 the reef, originally formed on the south coast lies, in the next stage, on the northern slope of the enlarged island, so that it is hardly permissible to speak of a more marked upheaval of the south coast. It may even be conceived that also *B* is situated north of the coastline of the new island, so that in that case the original island is covered entirely by the sea, while a new island has emerged farther south.

Elevated reefs of the Sermata group.

It has been said above that the reefs, formed at a certain epoch in the history of mountain building along the coasts of a geanticline, may perform various movements in the subsequent stages. The rate as well as the direction of the movement sometimes differ considerably at a comparatively short distance. This is clearly illustrated by the movements of the reefs in the period of development of the geanticline, in which only its highest parts emerge from the sea as a group of smaller islands. We shall dwell more particularly on the movements of the islands of Luang, Moa, Kisser, and Letti.

According to my observations in Luang this island, built up entirely of permian rocks, is together with two islets near the South-eastern extremity, fringed by a very broad reef, extending far in the direction of Sermata and also far to the West. Green islets far from the north coast and barren, dry portions far from the south coast, mark the limits in northern and southern direction; beyond them the sea floor declines rapidly. At ebb-tide part of the reef gets dry. Luang as well as the two islets close to it, to the South-east, rise up steeply from this broad reef; no trace of elevated reefs was detected, so that proofs of a period of upheaval are lacking. The island of Luang and the two islets near it, impress us as having originally formed one continuous whole, and as having been separated by a positive movement, which may also account for the formation of the broad encircling reef, which is bordered here and there by green islets. Post-glacial upheaval of the seasurface renders the subsidence of the land only apparent.

Now let us look at the island of Moa, more particularly its eastern half. For the most part the island consists of a low, very broad plateau of coral limestone, which rises scarcely more than 10—20 m. above the sea, and from which in the eastern part rises

the steep Kerbau mountain [1]), which consists entirely of peridotites. Traces of elevated reefs are lacking in the Kerbau mountain also, and if the eastern part of Moa were a little lower, this region would present an aspect similar to that of Luang. Both mountains, the Gg. Kerbau and the Bt. Merah would then emerge from the sea as two separate islands and be entirely fringed by a broad reef.

We feel justified in assuming that also the latter region has passed through a stage of evolution like that of Luang at the present day, and that it has been raised above the sea, through a slight upheaval after a period of subsidence or a long stationary period, or according to DALY through an upheaval after an apparent post-glacial subsidence. By this upheaval also the eastern part of Moa was united to the western part. In the latter elevated reefs are found at a greater height, so that the two united islands or group of islands have evidently been subject to markedly different movements.

The island of Kisser, typified by its peculiar form, behaved differently again. The more or less circular island, is surrounded on all sides by a wall of coral limestone raised in several (mostly five) terraces, and broken only by a few narrow gullies, through which rivulets flow towards the sea. We sighted this island only from the sea; according to VERBEEK [2]) the elevated reefs in the western part of the island, near Leweru, reach a height of 147 m., whereas the interior, where amphibolite hills prevail, presents peaks ± 240 m. high. The terraced structure of the elevated reefs points to an elevation of the island, repeatedly interrupted by intervals of quiescence or — considering the thickness of the elevated reefs (to 80 m.) — of subsidence, by which a reefcap was formed, strong enough to resist erosion.

The island of Letti presents quite a different appearance nowadays from that of Kisser, but most likely this island has also been encircled by a more or less continuous girdle of fringing reefs, of which at larger heights occasional remainders were left at 115, 129 and 134 m. [3]) above sealevel. Here erosion has demolished the higher reefs almost entirely, which — on the basis of what we observed about the influence of erosion — may have something to do with long and uninterrupted negative movements.

Many more examples of numerous abnormal elevated reefs in the

[1]) H. A. BROUWER. Geologie van een gedeelte van het eiland Moa. Jaarb. v. h. Mijnwezen Verhandel. 1916. I, p. 39.

[2]) R. D. M. VERBEEK, l. c., p. 432.

[3]) G. A. F. MOLENGRAAFF and H. A. BROUWER. De geologie van het eiland Letti. Jaarb. Mijnwezen. 1914. Verh. I, p. 82.

neighbouring islands could be adduced, but the foregoing sufficiently shows that the evolution of the geanticline has evolved during the mountain building process very irregular movements at a comparatively short distance.

Tilting Islands.

Among those we reckon e.g. the island of Misool, to the North of Ceram. Corals are thriving well, as well on the south- as on the northcoast, but elevated coral reefs occur only in the flat northern part of the island, whereas they are lacking entirely along the steeper south coast up to some way past the watershed. The island may be said to have tilted, if we assume that the south coast has subsided along the line of a fault at the same time when the north coast has moved upwards. This should seem to be very likely especially with the island of Misool, because WANNER [1]) has established the presence of a number of faults in the archipelago along the south coast bordering on the north side of the deep sea-basin between Misool and New Guinea on the one side and Ceram on the other.

However, similar reef-formations may also originate in another way, where tilting is out of the question, because the movement is not performed by the island as such, but because in the initial and the terminal stage different parts of a developing geanticline present themselves as islands. In Fig. 1 we have only to look upon the geanticline in $P^1 B^1 Q^1$ as the initial stage and in PBQ as the terminal stage. In the latter the geanticline has subsided deeper below the sea-surface, but on the north coast an upraised reefcap will be seen. With rising geanticlines a similar distribution of the elevated reefs will also be seen, e.g. in the manner illustrated in Fig. 2.
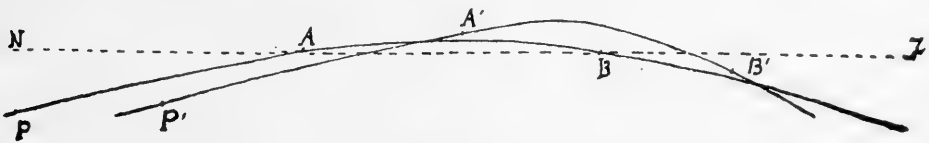

Fig. 2.

In the terminal stage $P'A'B'$ only upraised reefs will occur on the north side of the new island, viz. between A' and the north coast. Then the island is not merely tilted, but exhibits that part of a rising geanticline, which at a certain time emerges from the sea.

[1]) J. WANNER. Beiträge zur geologischen Kenntniss der Insel Misol, Tijdsch. Kon. Ned. Aardrijksk. Gen. 1910, p. 498.

CONCLUSIONS.

1. The parts of a reefcap formed during negative movements may for two reasons disappear rapidly through erosion. Considerable gaps in the development of a reefcap may, therefore, suggest long and uninterrupted negative movements.

2. In the case of geanticlines, raised above the sea over extensive areas, observations along the coast cannot lead to conclusions about the movements of the highest points, — also with a stable sealevel.

3. The development of the geanticline causes reefs of the same age to rise to various heights, which sometimes differ considerably.

4. The highest parts of a reefcap are not on that score the oldest, also when faulting is left out of consideration.

5. At the top of a moving geanticline an island may disappear and yet an island remains visible.

6. Islands may tilt or only exhibit the semblance of doing so.

Physics. — *"On the Occurrence of Solid Substance in Binary Mixtures with Unmixing"* I. By Prof. F. E. C. Scheffer. (Communicated by Prof. J. Böeseken).

(Communicated in the meeting of November 30 1918).

1. *Introduction.* When two phases coexist in a binary system, the condition that the temperature and the three quantities $\left(\dfrac{d\psi}{dv}\right)_{xT}$, $\left(\dfrac{d\psi}{dx}\right)_{vT}$, and $\psi - v\left(\dfrac{d\psi}{dv}\right)_{xT} - x\left(\dfrac{d\psi}{dx}\right)_{vT}$ shall be equal for the two phases, must be satisfied. On the surface $\psi = f(v, x)$, constructed for a definite temperature, the coexisting phases are obtained by rolling a bi-tangent plane over this surface. Another method to find the coexisting phases consists in this that the system of curves $\left(\dfrac{d\psi}{dv}\right)_{xT} =$ = constant (p-lines), $\left(\dfrac{d\psi}{dx}\right)_{vT} =$ constant (q-lines) and $\psi - v\left(\dfrac{d\psi}{dv}\right)_{xT} - x\left(\dfrac{d\psi}{dx}\right)_{vT} =$ constant (potential lines) are thought to be traced projected on the $v - x$ plane; then two points on the ψ-surface indicate coexisting phases when through the projections of these points run a same p-line, a same q-line, and a same potential line.

The points indicating coexisting phases, furnish in the $v - x$-projection a locus the inclination of which is determined by:

$$\left(\frac{dv_1}{dx_1}\right)_{bin} = -\frac{(v_2-v_1)\dfrac{d^2\psi}{dv_1 dx_1} + (x_2-x_1)\dfrac{d^2\psi}{dx_1^2}}{(v_2-v_1)\dfrac{d^2\psi}{dv_1^2} + (x_2-x_1)\dfrac{d^2\psi}{dv_1 dx_1}}, \quad \cdot \quad \cdot \quad (1)$$

in which the indices 1 and 2 refer to the two coexisting phases [1]).

The indicatrix in a point of the ψ-plane is given in first approximation by the equation:

$$v^2\frac{d^2\psi}{dv_1^2} + 2vx\frac{d^2\psi}{dv_1 dx_1} + x^2\frac{d^2\psi}{dx_1^2} + \alpha v + \beta x + \gamma = 0 \quad \cdot \quad \cdot \quad (2)$$

[1]) Van der Waals—Kohnstamm. Thermodynamik. II. S. 196, equation 1.

When equation (1) is written in the form:

$$\left(\frac{dv_1}{dx_1}\right)_{bin} \frac{v_2-v_1}{x_2-x_1}\frac{d^2\psi}{dv_1{}^2} + \left[\left(\frac{dv_1}{dx_1}\right)_{bin} + \frac{v_2-v_1}{x_2-x_1}\right]\frac{d^2\psi}{dv_1 x_1} + \frac{d^2\psi}{dx_1{}^2} = 0,. \quad (3)$$

it appears from (2) and (3) that the binodal line and the nodal line represent conjugate diameters in the indicatrix, which has been demonstrated by KORTEWEG [1]).

2. *The Relative Situation of Binodal Lines and Nodal Lines.*

A great number of inferences which are of importance for the treatment of the more intricate cases of heterogeneous equilibrium, which may present themselves for binary mixtures, may be made from the above mentioned conclusions from the theory of binary mixtures, which have been known already for a long time.

We shall imagine *two* binodal lines going through a point of the ψ-plane; each binodal line with the nodal line belonging to it is a set of conjugate diameters in the indicatrix. Depending on the form of the indicatrix we now get the following cases:

$a.$ $\dfrac{d^2\psi}{dv^2}\cdot\dfrac{d^2\psi}{dx^2} > \left(\dfrac{d^2\psi}{dv\,dx}\right)^2.$ *Elliptical point.*

From the well-known thesis of the ellipse that two pairs of conjugate diameters separate each other, follows when we indicate the direction of the tangents to the binodal lines, by b_1 and b_2, that of the nodal lines by n_1 and n_2:

Moving in a definite direction round the elliptical point, the succession of binodal and nodal lines is:

$$b_1\ b_2\ n_1\ n_2.$$

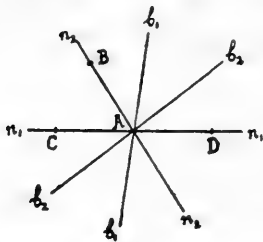Now the two phases coexisting with A (fig. 1) can:

1. form a three-phase triangle ABC, so that the two binodal lines lie entirely outside the triangle, and

2. form a three-phase triangle ABD, so that the two binodal lines lie on one side of A within the triangle.

As, however, binodal lines within the triangle indicate two-phase coexistences which are metastable with regard to the third phase (the three phase equilibrium is, namely, stable inside the three-phase triangle [2]), it appears that the above mentioned conclusion can also be expressed in the following words:

Fig. 1.

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[1]) KORTEWEG. Arch. Néerl. **24**, 57 and 295 (1891).

[2]) We assume that there occur no points on the ψ-surface where the surface seen from below is concave-concave.

When one of the phases participating in the three-phase equilibrium corresponds with an elliptic point on the ψ-surface, the prolongations of the (stable) binodal lines lie either both inside or both outside the three-phase triangle.

b. $\dfrac{d^2\psi}{dv^2} \cdot \dfrac{d^2\psi}{dx^2} = \left(\dfrac{d^2\psi}{dv.dx}\right)^2$. *Parabolical point.*

From equation (1), which can easily be transformed into:

$$\left(\frac{dv_1}{dx_1}\right)_{bin} = -\frac{(v_2-v_1) + (x_2-x_1)\dfrac{\dfrac{d^2\psi}{dx_1^2}}{\dfrac{d^2\psi}{dv_1 dx_1}}\dfrac{d^2\psi}{dv_1 dx_1}}{(v_2-v_1) + (x_2-x_1)\dfrac{d^2\psi}{dv_1 dx_1}\dfrac{d^2\psi}{dv_1^2}} \quad \cdots \quad (4)$$

and from $\left(\dfrac{d\psi}{dv}\right)_x = -p = \text{constant}$ and $\left(\dfrac{d\psi}{dx}\right)_v = q = \text{constant}$, for which the following relations are valid:

$$\left(\frac{dv_1}{dx_1}\right)_p = -\frac{\dfrac{d_2\psi}{dv_1 dx_1}}{\dfrac{d^2\psi}{dv_1^2}} \quad \text{and} \quad \left(\frac{dv_1}{dx_1}\right)_q = -\frac{\dfrac{d^2\psi}{dx_1^2}}{\dfrac{d^2\psi}{dv_1 dx_1}},$$

follows that equation (4) for a parabolic point reduces to:

$$\left(\frac{dv}{dx}\right)_{bin} = \left(\frac{dv}{dx}\right)_p = \left(\frac{dv}{dx}\right)_q.$$

Hence the two binodal lines touch the p- and the q-lines, and accordingly they are in contact with each other; the two nodal lines form arbitrary angles with the binodal lines and also with each other.

When one of the phases participating in the three-phase equilibrium corresponds with a parabolic point on the ψ-surface, there is contact between the two binodal lines; the binodal lines either lie partly inside or entirely outside the three-phase triangle.

c. $\dfrac{d^2\psi}{dv^2} \cdot \dfrac{d^2\psi}{dx^2} < \left(\dfrac{d^2\psi}{dvdx}\right)^2$. *Hyperbolical point.*

In a hyperbola pairs of conjugate diameters do not separate each other. Hence:

Moving in a definite direction round a hyperbolical point, the order of binodal lines and nodal lines is:

$$b_1\ b_2\ n_2\ n_1 \quad \text{or} \quad b_1\ n_2\ b_2\ n_1 .$$

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When the triangle in fig. 2a (order $b_1\,b_2\,n_2\,n_1$) is represented by ABC, the two binodal lines lie entirely outside the triangle, when by ABD, they lie both partly inside it, whereas in fig. 2b (order $b_1\,n_2\,b_2\,n_1$) one binodal line lies partly inside, one entirely outside the triangle both for the three-phase equilibrium ABC and for ABD.
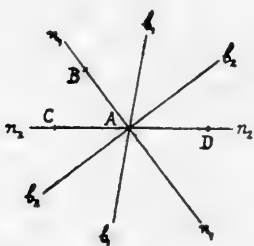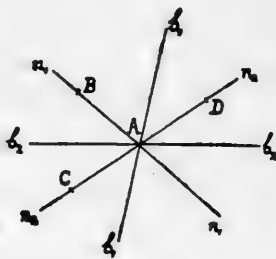

Fig. 2a.   Fig. 2b.

3. Of the conclusions discussed in § 2 the last of those mentioned under a is not new. Some years ago Kuenen proved this thesis by another method [1]). I think I have demonstrated in what precedes that the relative situation of nodal lines and binodal lines can directly be derived in a general way from the already long known properties of the ψ-surface [2]).

Though the realizable parts of the ψ-surface are only indicated by elliptical points, the general discussion of § 2 has the advantage that it points out a regularity for the whole ψ-surface. The above discussed conclusions are of great importance when we want to examine the possible coexistences of solid by the side of fluid. By the aid of the rules discussed in § 2 it is possible to indicate the relative situation of the binodal lines solid-fluid and fluid-fluid in every point. They are almost indispensable in this study, because when these rules are not observed, we are often in danger in the more intricate cases of mistaking impossible cases for possible ones, especially in the metastable and unstable region. And for a complete survey of these existences the not realizable parts of the ψ-surface cannot be dispensed with.

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[1]) Kuenen. These Proceedings. XIV p. 420.

[2]) *Note added during the correction of the Dutch proofs.* The theses of § 2 are not only valid for the ψ-surface, but for any surface, hence also for the ζ-surface. In Bakhuis Roozeboom's Heterogene Gleichgewichte III. 2. Schreinemakers thus discusses analogous rules (p. 115 et seq.); the situations in the metastable region have, however, been only partly treated (p. 340 et seq.).

4. *Coexistence of Solid by the Side of Fluid Phases.*

When the curves CD and EF in fig. 3 represent projections of binodal lines of a plait on the ψ-surface, the v—x-plane is divided into six regions by the nodal-lines AB and the tangents to the binodal lines in A and B. When also a solid phase S coexists with A and B, the point representing the solid phase can lie in each of these regions. Then the rules of § 2 easily give the course of the binodal line through A and B for fluid phases existing by the side of solid
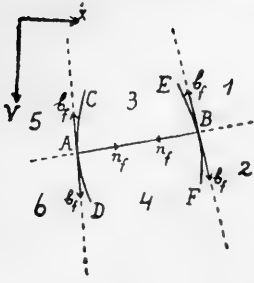
Fig. 3.

for each of these cases. When the solid substance is the second component, the most frequently occurring situations are those of the regions 2 and 1. The first case is represented in fig. 4a, the second in fig. 5a; the plait has been assumed to be stable for both, i. e. to lie on the convex-convex part of the ψ-surface (seen from below).
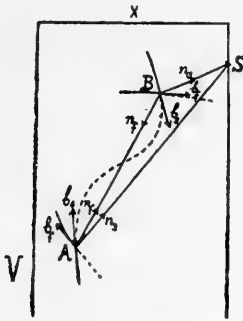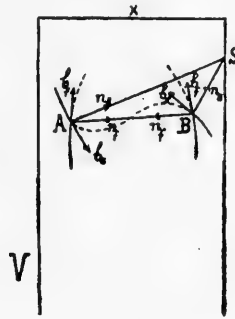
Fig. 4a.   Fig. 5a.

The points A and B are, therefore, elliptical, and the rules of § 2a determine the situation of the binodal line for fluid phases coexisting with solid in the two points, as it has been indicated in figs. 4a and 5a. These situations correspond to the P-x-figures indicated in figs. 4b and 5b, in which the three-phase coexistence is again indi-
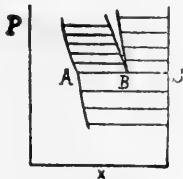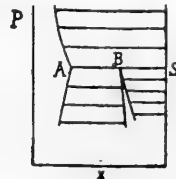
Fig. 4b.   Fig. 5b.

cated by ABS, and the two-phase regions are hatched; the hatching-lines indicate nodal lines.

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The transition case which causes fig. 4a to pass into fig. 5a now also often occurs for the practically occurring heterogeneous equilibria. (An instance of this is discussed in § 6). When namely the point S lies on the prolongation of the line AB, the nodal lines n_s and n_f coincide (n_s is the nodal line drawn from a fluid to the solid phase, n_f to the other fluid phase). The theorem of § 2a then requires that also b_s and b_f coincide, in other words that the two binodal lines are in contact.

When a solid phase lies on a nodal line of the fluids, the binodal lines fluid-fluid and fluid-solid touch each other in the nodes.

In a perfectly analogous way it also follows that:

If the nodal line solid-fluid touches the binodal line fluid-fluid, the binodal line solid-fluid touches the nodal line of the fluid phases.

All the cases that can occur for a stable plait, have now been discussed. It, however, repeatedly occurs that part of the plait indicates unstable states; in the points of the binodal lines which are situated within the spinodal line the surface is namely convex-concave, and the points themselves are hyperbolical. In analogy with figs. 4a and 5a we can now again construct two figures, which are applicable when one of the binodal lines consists of hyperbolical points. (The case, that both binodal lines consist of hyperbolical points is not considered; the discussion is self-evidently just as simple). In these cases we get figs. 6 and 7. In both point A is
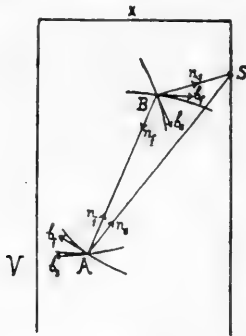
Fig. 6.   Fig. 7.

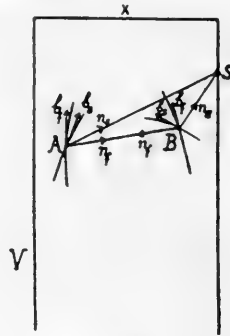given as hyperbolical, point B as elliptical point. The corresponding P-x-diagrams are easy to construct; they have, therefore, been omitted; besides the coexistences are not realizable, and are accordingly devoid of practical importance.

5.   *The Four-Phase Equilibria.*

When on the ψ-surface simultaneous coexistence with solid occurs for a three-phase equilibrium of fluid phases, the number of nodal

lines and binodal lines passing through the nodes, amounts to three. When we assume that the three-phase coexistence takes place on the stable part of the ψ-surface, the three fluid phases participating in this equilibrium are indicated by elliptical points; the relative situation of the three pairs of conjugate diameters is again determined by the rules of § 2*a* in this sense that these theorems hold good for every combination in sets of two of the 3 pairs of conjugate diameters.

6. *Applications*.

In a treatise on the phenyl- and tolylcarbaminic acids recently published in these Proceedings it was pointed out that the different P-T-figures which are found for these homologous compounds, can be derived from each other by moving the quadruple point along the three-phase line $L_1 L_2 G$[1]). When the quadruple point reaches the critical endpoint, it is still just stable; this is the transition case, which connects this type of binary systems with the type sulphuretted hydrogen-ammoniac, where the coexistence $L_1 L_2 G$ does not appear stable any more.

Such a transition is also found for binary systems without compound, a fact which Büchner[2]) already pointed out in his Thesis for the Doctorate. We then get a transition from a system with a quadruple point to the type diphenylamine-carbonic acid. The transition itself has not been studied by Büchner; as it is, however, possible that by a suitable choice of the components we can get close to this transition case — in the cited paper I drew attention to the system as-o-xylidine-carbonic acid — the study of this transition case has probably not only theoretical importance.

This transition can now be simply followed by the aid of the rules mentioned in §§ 1—5; it has, indeed, been the study of this transition that induced me to seek the regularities mentioned in what precedes.

A complete discussion of this transformation is not possible with the aid of the above rules alone. For these only indicate the course of binodal and nodal lines in the neighbourhood of the nodes. Yet this is already sufficient to give us an insight into the phenomena that will make their appearance in this transition case.

For this purpose I will imagine the ψ-surface to be constructed for the temperature of the critical endpoint ($L_1 = G$). We may then expect a situation as indicated by fig. 8*a* or 8*b*. The plaitpoint P_1

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[1]) These Proceedings. **21**. 664. (1919).

[2]) Büchner. Thesis for the Doctorate. Amsterdam 1905.

represents L_1 and L_2 becoming identical, P_3 represents L_1 and G
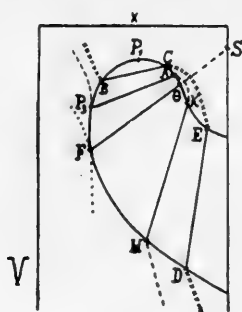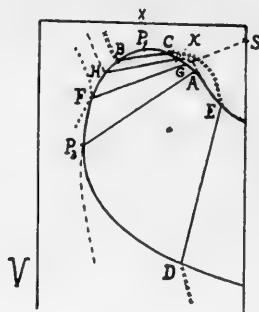

Fig. 8a.   Fig. 8b.

becoming identical; the plait of P_3 has disappeared in this last point within the longitudinal plait; it has been omitted for the sake of the lucidity of the figures. The liquid coexisting with the fluid phase P_3 is indicated by A. The nodal lines BC in the plait P_3P_1A present a situation corresponding to fig. 5a; the nodal lines DE to fig. 4a. It follows from this that a nodal line may be drawn between BC and DE, the prolongation of which passes through S (FG in the figs. 8a and 8b). Hence in the points F and G a possibly occurring binodal line for fluid phases coexisting with solid touches the binodal line fluid-fluid. (See § 4). In fig. 8a the nodal line FG lies below P_3A, in fig. 8b it lies above it.

When we now inquire into the course of the binodal line solid-fluid, all the possible situations can be easily surveyed by rolling a tangent plane for continually decreasing values of ψ_s over the surface. When the ψ-value of S is chosen high, the tangent curve will only intersect the plait on the righthand of DE; with lower value of ψ_s a curve will make its appearance which also passes through P_1; further the curve will intersect the plait both in the neighbourhood of P_1 and in the neighbourhood of DE. Such a situation is represented by the curve indicated by crosses. When ψ_s is made to shift further, we get a curve passing through P_3 indicated by a line of dashes. Finally the tangent curve will move in such a way that the two points of intersection on the two binodal branches approach each other, and at the coincidence in F and G contact of the two binodal curves takes place; the curve for solid-fluid lies in F outside the binodal line fluid-fluid and is stable; for G it lies, however, in the covered region. By the aid of the rules of § 2 it may be derived that the traced situations are the correct ones. It should, however, be pointed out that according to these rules the binodal lines in P_3 touch and intersect.

The three binodal lines for solid-fluid indicated in the two figures correspond to the equilibria marked by the same letters in figs. $9a$ and b. It will be clear from what has been discussed that the point
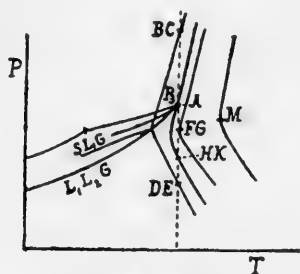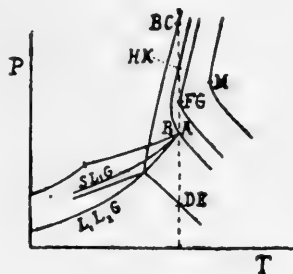

Fig. 9a.   Fig. 9b.

where $\dfrac{dP}{dT} = \infty$, may lie both at higher and at lower pressure than P_s[1]). This point corresponds to a nodal line (FG) passing through S in figs $8a$ and $8b$. On still further displacement the binodal curve for solid lies outside the longitudinal plait. Then the point of contact can appear at higher temperature; in figs, $9a$ and b such a point of contact is indicated by M. The situation of the three-phase line passing through M has been found experimentally by BÜCHNER in the system diphenylamine-carbonic acid[2]), by ADA PRINS in the system ethane-naphtalene[3]).

7. The transition of the systems with quadruple point $SL_1\ L_2G$ to the type diphenylamine-carbonic acid has been derived in the preceding paragraph by the aid of the rules given in § 2. The shape of the binodal curves is indicated by them, however, only in the neighbourhood of the points of intersection. The course throughout the region, which is remarkable especially in the covered region, could be dispensed with in the above discussion. A full insight can only be obtained by considerations on the course of binodal lines solid-fluid in general. For this the discussion of some loci on the ψ-surface is required.

(*To be continued.*)

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[1]) At lower temperatures this point lies in the covered region; it will appear on a fuller treatment of the transformation that the displacement of this point follows easily from the transition of the two three-phase lines SL_1L_2 and SL_2G into each other (unstable ridge), and the change in this on approach to the critical endpoint. These changes may also be directly examined by the aid of the rules of § 2.

[2]) BÜCHNER. Thesis for the Doctorate. Amsterdam. 1905, p. 85, fig. 36.

[3]) ADA PRINS. These Proc. XVII p. 1095.

Physics. — *"On the shape of large liquid drops and gas-bubbles and the use made of them for the measurement of capillary constants."* By Prof. J. E. VERSCHAFFELT. Supplement N°. 43a to the Communications from the Physical Laboratory at Leiden. (Communicated by H. KAMERLINGH ONNES.)

(Communicated in the meeting of November 30, 1918).

§ 1. The meridional section of the capillary surface in the case of a surface of revolution is determined by the well-known equation

$$\frac{1}{x}\frac{d\,(x\,\sin\varphi)}{dx} = k\,(h+y) = kz\ ^1), \qquad \cdots \cdots \quad (1)$$

which on account of the relation $\tan\varphi = \dfrac{dy}{dx} = \dfrac{dz}{dx}$ can also be written in the form:

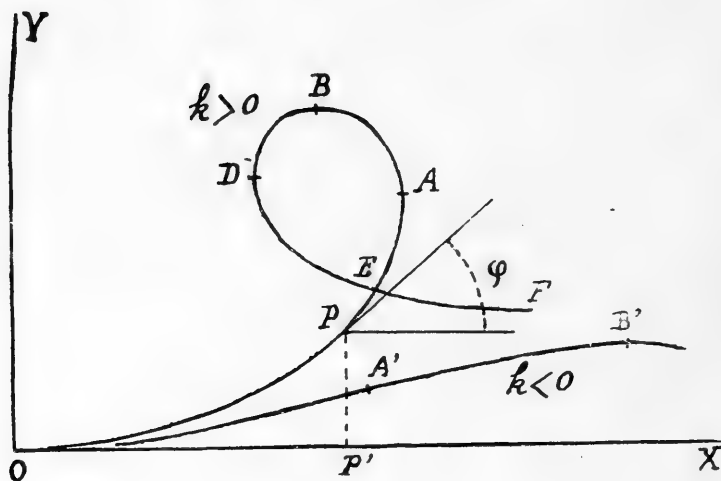$$kz\,dz = \sin\varphi\,d\varphi + \frac{\sin\varphi}{x}\,dz \qquad \cdots \cdots \quad (1')$$

Fig. 1.

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¹) Compare: 'On the shape of small drops and gas-bubbles". Leiden Comm. Suppl. N°. 42c (1918): these Proc. XXI (1) p. 357.

Fig. 1 gives a diagrammatic representation of the meridional section of the capillary surface for $k = \dfrac{(\mu_1-\mu_2)g}{\sigma} > 0$ and for $k < 0$, in the case that R_0 (the radius,

We shall first assume, that $k > 0$ (liquid below the surface, at least in the neighbourhood of the axis), as is the case in a wide tube or with a drop lying on a surface.

§ 2. When the meniscus is very large, it will be practically flat near the axis and the curvature of the surface is only appreciable near the edge. This naturally suggests, for the purpose of integrating equation 1', dividing the curve into two portions: a central part, where the angle φ obtains but small values and which extends to pretty near the edge, and a marginal part, where φ can assume larger values and which for smaller values of φ passes into the central portion.

Let l be a special value of x belonging to the marginal part (for which we shall take the abscissa of point B in fig. 1). If l is sufficiently large, it is clear that the marginal part of the curve cannot differ much from what would be found in the two-dimensional problem $(l = \infty)$; the width of the marginal part is then small as compared to l (cf. § 3), whence putting $x = l + u$, u may be treated as small with respect to l[1]). For that part we may therefore write

$$kz\, dz = \sin \varphi \, d\varphi + \frac{1}{l}\sin \varphi \left(1 - \frac{u}{l} + \dots \right) dz, \quad . \quad . \quad (2)$$

which equation may be solved by successive approximations.

§ 3. To a first approximation we thus have, as in the two-dimensional problem[2]), since z and φ become very small together[3]) and $u = 0$ for $\varphi = \pi$,

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of curvature at the top) is very large compared to x, i.e. that $R_0 \sqrt{\pm k}$ is a large number and therefore $h\sqrt{\pm k} = \dfrac{2}{R_0 \sqrt{\pm k}}$ a small number.

The figure is drawn on the assumption of R_0 being positive (i.e. liquid below for $k > 0$ and above for $k < 0$); in the opposite case the meridional curve would be obtained by turning the figure over about the x-axis.

[1]) This method of simplifying the problem was already used by Poisson, Nouvelle théorie de l'action capillaire. See also: A. Ferguson, Phil. Mag., (6), 25, (1913) p. 507.

[2]) Compare for instance A. Winkelmann, Handbuch der Physik, 2e Aufl I (2), (1908) p. 1131.

[3]) z does not become zero, however, for $\varphi = 0$; from which it would seem to follow that equations (3) can only hold as long as φ is not infinitely small. On closer inspection they appear to remain valid (provided $u < < h$), since the dependence of z on x for small values of z is of an exponential nature; indeed, for φ small (3) gives $u\sqrt{k} = \log \varphi + 2 - \log 4 = \log \varphi + 0,614$, $z\sqrt{k} = \varphi = = 0,543\, e^{u\sqrt{k}} = 0,543\, e^{-l\sqrt{k}} \cdot e^{x\sqrt{k}}$; hence the minimum-value which z attains at a large distance from the edge is infinitely small of a higher order than the infinitely small values of z in the neighbourhood of the edge.

$$z \sqrt{k} = 2 \sin \tfrac{1}{2} \varphi \text{ }^1) \qquad u \sqrt{k} = \log \tan \tfrac{1}{4} \varphi + 2 \cos \tfrac{1}{2} \varphi \text{ }^2). \quad . \quad (3)$$

Substituting this value of z in the first correction-term of (2) we obtain as a second approximation

$$\tfrac{1}{2} kz^3 = 2 \sin^3 \tfrac{1}{2} \varphi + \frac{4}{3l \sqrt{k}} (1 - \cos^3 \tfrac{1}{2} \varphi) \quad . \quad . \quad . \quad (4)$$

or, as long as $\sin \tfrac{1}{2} \varphi$ does not become infinitely small $(\varphi < 2 \pi)^3)$

$$z \sqrt{k} = 2 \sin \tfrac{1}{2} \varphi + \frac{1}{3l \sqrt{k}} (2 \tan \tfrac{1}{4} \varphi + \sin \varphi)\text{ }^4) . \quad . \quad (4')$$

$$u \sqrt{k} = \log \tan \tfrac{1}{4} \varphi + 2 \cos \tfrac{1}{2} \varphi + \frac{1}{3l \sqrt{k}} (\tfrac{3}{2} \log \tan \tfrac{1}{4} \varphi - \tfrac{1}{4} \sec^2 \tfrac{1}{4} \varphi + \cos \varphi + \tfrac{3}{2}) \quad (5)$$

Putting φ successively equal to $\dfrac{\pi}{2}$, π and $\dfrac{3\pi}{2}$ the coördinates of A, B and D (fig. 1) are found as follows:

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[1] In order that this expression may stand as a first approximation, $\dfrac{1}{l} \sin \varphi$ must be very small as compared to kz or, since $\sin \varphi$ is 1 at the utmost, klz must be a large number $(klz \gg 1)$; it follows, introducing the expression for z and remembering that also $\sin \varphi < $ or $= 1$, that $2l\sqrt{k} \gg 1$. $2l\sqrt{k}$ must therefore be a large number, say 100; since for water k is about 13, l has to be at least 15 cms in order that the approximation may be applicable. For mercury $(k = 30)$ it would be 10 cms.

[2] From this relation it follows, that φ may be considered as infinitely small, while u itself is still small with respect to l; i.e. φ actually becomes very small in the marginal part (provided $l\sqrt{k} \gg 1$). For instance for $\varphi = \text{}^1/_{100}$ ($0°.6$ about) $u\sqrt{k}$ becomes approximately $- 4$, i.e. still a moderate number; in view of this fact, however, the practical limit of applicability of the approximation was possibly estimated still rather low at $l\sqrt{k} = 50$.

[3] Unless φ itself is infinitely small, for in that case the correction term in (4) is still much smaller than the principal term.

[4] Except for a small reduction this formula was already given by POISSON (loc. cit.). With the degree of approximation in question it is of no importance that the quantity l has not the same meaning with POISSON as here, the difference being small compared to l itself; indeed we might just as well have represented by l any other distance which differs from l by an infinitely small amount, such as the abscissa of A or of D (fig. 1).

Compare also FERGUSON, loc. cit., equation IX, where, however, the expression for $z\sqrt{k}$ is incorrect owing to an error of sign.

It may be here remarked in passing, that the manner in which FERGUSON integrates equation (2) comes to the same as introducing a new variable $c = l\varphi + z$; for the rest the equation is also solved by successive approximations. The transformation in question is unnecessarily cumbrous.

$$\varphi_A = \frac{\pi}{2} \quad z_A \sqrt{k} = \sqrt{2} + \frac{1}{3l\sqrt{k}}(2\sqrt{2}-1) = 1{,}414 + \frac{0{,}609}{l\sqrt{k}}$$

$$u_A\sqrt{k} = log(\sqrt{2}-1) + \sqrt{2} + \frac{1}{6l\sqrt{k}}\{3log(\sqrt{2}-1) + \sqrt{2} + 1\} = 0{,}532 - \frac{0{,}039}{l\sqrt{k}} \quad (6)$$

$$\varphi_B = \pi \quad z_B\sqrt{k} = 2 + \frac{2}{3l\sqrt{k}} \qquad u_B\sqrt{k} = 0 \quad . \quad . \quad . \quad (7)$$

$$\varphi_D = \frac{3\pi}{2} \quad z_D\sqrt{k} = \sqrt{2} + \frac{1}{3l\sqrt{k}}(2\sqrt{2}+1) = 1{,}414 + \frac{1{,}276}{l\sqrt{k}}$$

$$u_D\sqrt{k} = log(\sqrt{2}+1) - \sqrt{2} + \frac{1}{6l\sqrt{k}}\{3log(\sqrt{2}+1) - (\sqrt{2}-1)\} \quad (8)$$

$$= -\{log(\sqrt{2}-1) + \sqrt{2}\} - \frac{1}{6l\sqrt{k}}\{3\,log(\sqrt{2}-1) + (\sqrt{2}-1\} = -0{,}532 + \frac{0{,}372}{l\sqrt{k}}$$

We shall not try to carry on the approximation any further.

§ 4. We now come to the central part of the meridional curve. Since in that part φ is infinitely small, we may put $sin\,\varphi = \varphi = tan\,\varphi = z'$, and may thus write equation (1) to a first approximation in the form

$$\frac{1}{x}\frac{d}{dx}(xz') = kz \quad or \quad z'' + \frac{z'}{x} - kz = 0 \quad . \quad . \quad . \quad (9)$$

By the substitution $ix\sqrt{k} = \xi$, $z = \eta$, the equation reduces to

$$\eta'' + \frac{\eta'}{\xi} + \eta = 0, \quad . \quad . \quad . \quad . \quad . \quad (9')$$

which is BESSEL's equation of order zero. Therefore, considering that at $x = 0$ z is finite, we have

$$z = h\,J_0(ix\sqrt{k}), \quad . \quad . \quad . \quad . \quad . \quad (10)$$

J_0 being BESSEL's function of the 1st kind and order 0; the integration-constant h is equal to the value of z for $x = 0$[1]).

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[1]) Since $J_0(\xi) = 1$ for $\xi = 0$. Consequently for a very large meniscus (very large R_0) in the neigbourhood of the axis of rotation, replacing h by its value $\dfrac{1}{2kR_0}$ (cf. Leiden Comm. Suppl. N⁰. 42c; these Proc. XXI (1) p. 357)), we have

$$z = \frac{1}{2k\,R_0}\left\{1 + \frac{1}{(1\,!)^2}\frac{kx^2}{4} + \frac{1}{(2\,!)^2}\left(\frac{kx^2}{4}\right)^2 + \ldots\right\},$$

as is also found directly by solving the differential equation of the meridional section by development in a series (cf. SCHALKWIJK, Leiden Comm. N⁰. 67, (1900 – 1901) these Proc. III, p. 421, 481) and putting $R_0 = \infty$.

§ 5. It follows from (10)[1]), that for large values of x differing little from l ($x = l + u$)

$$z = h \frac{e^{x\sqrt{k}}}{\sqrt{2\pi x}\sqrt{k}} = \frac{h}{\sqrt{2\pi}} \frac{e^{l\sqrt{k}} e^{u\sqrt{k}}}{\sqrt{l}\sqrt{k}} \left(1 - \tfrac{1}{2}\frac{u}{l}\right) \quad . \quad . \quad . \quad (11)$$

On the other hand it follows from (4′) and (5), that for infinitely small values of φ, but x still differing little from l,

$$log\, z \sqrt{k} = log\, \varphi = u\sqrt{k} - (2 - log\, 4) - \frac{u}{2l} \quad . \quad . \quad . \quad (12)$$

By equating the values of z in (11) and (12), putting $x_A = r$ and remembering, that $r\sqrt{k} - l\sqrt{k} = u_A\sqrt{k}$ (eq. 6), we find

$$h\sqrt{k} = 0{,}924 \sqrt{2\pi r \sqrt{k}}\, e^{-r\sqrt{k}} \quad . \quad . \quad . \quad . \quad (13)$$

This therefore is the relation between the radius r of a wide tube and the ascension h of the liquid in the tube (the angle of contact being zero).

§ 6. An examination of the further course of the meridional curve at a larger distance from the axis than $x = l$ (branch DEF... etc.) shows, that the curve consists of a series of U-shaped curves, as represented diagrammatically in WINKELMANN's Handbuch der Physik, I (2) p. 1141, fig. 404; these curves, however, are very much
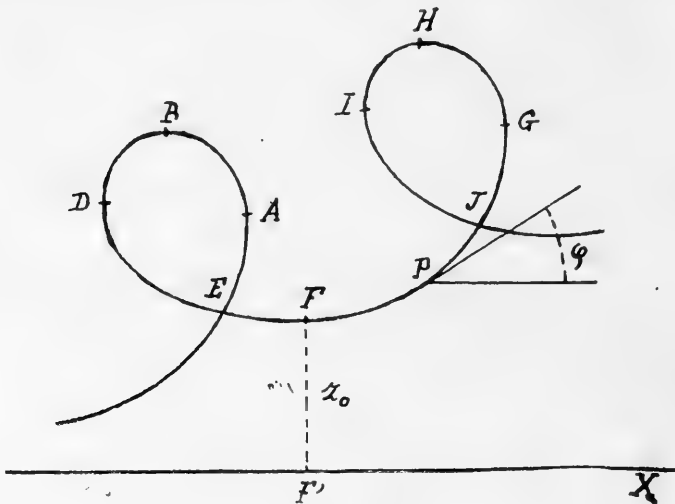

Fig. 2.

elongated as shown in fig. 399 on p. 1135. The width of the curves is small compared to l; they therefore still belong to the marginal part of the meridional curve and the equation to these curves is

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[1]) See for instance NIELSEN, Handbuch der Theorie der Cylinderfunktionen, 1904, p. 156.

found in the same manner as equation (4). Representing by $z_{\bullet}$ the minimum of z (ordinate of the lowest point F, fig. 2) and putting $\varphi = 0$ for $z = z_0$ we find

$$k (z^2 - z_0{}^2) = 4 \sin^2 \tfrac{1}{2} \varphi \pm \frac{8}{3l \sqrt{k}} (1 - \cos^2 \tfrac{1}{2} \varphi) \quad . \quad . \quad . \quad (14)$$

(the positive and negative signs corresponding to $\varphi > 0$ and $\varphi < 0$ respectively) [1]). Since the curves have to join on to each other, it is easily found, that for the nth curve

$$z_0 \sqrt{k} = \frac{4 \sqrt{n}}{\sqrt{3l \sqrt{k}}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where the abscissa of F may conveniently be taken for l.

Putting $\Delta \psi = \sqrt{1 - \lambda^2 \sin^2 \psi}$, where $\lambda^2 = \dfrac{4}{4 + k z_0{}^2}$ and $\psi = \tfrac{1}{2} (\pi + \varphi)$, we have as a first approximation, as in the two-dimensional problem [2]),

$$z \sqrt{k} = 2 \Delta \psi \qquad u \sqrt{k} = \int_{1/2\pi}^{\psi} \frac{d\psi}{\Delta \psi} - 2 \int_{1/2\pi}^{\psi} \Delta \psi \, d\psi, \quad . \quad . \quad (16)$$

u being the abcissa of an arbitrary point P of the curve relatively to point F, i.e. $u = x_P - x_F$; the total width $2p$ of the curve is therefore such that

$$2p \sqrt{k} = (x_H - x_B) \sqrt{k} = 2 (K - 2 E), \quad . \quad . \quad . \quad (17)$$

K and E being the complete elliptical integrals $\left(\displaystyle\int_0^{1/2\pi} \right)$ of the 1st and 2nd kind respectively, with modulus λ. Now λ is but little smaller than 1, viz.

$$\lambda = 1 - \tfrac{1}{8} k z_0{}^2 = 1 - \frac{2n}{3l \sqrt{k}}; \quad . \quad . \quad . \quad . \quad . \quad (18)$$

K is therefore very large, namely in a first approximation [3])

$$K = \log \frac{4}{\sqrt{2 (1 - \lambda)}} = \tfrac{1}{2} \log 8 - \tfrac{1}{2} \log \frac{2n}{3l \sqrt{k}} \quad . \quad . \quad . \quad (19)$$

E being finite, viz. $= 1$; it follows that

$$z_{\bullet} \sqrt{k} = 1{,}082 \, e^{-p\sqrt{k}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

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[1]) The change of sign at $\varphi = 0$ is due to the change of sign of $\sin \tfrac{1}{2} \varphi$, whence for $\varphi > 0$ $\sqrt{k(z^2 - z_0{}^2)} = + 2 \sin \tfrac{1}{2} \varphi$ and for $\varphi < 0 = - 2 \sin \tfrac{1}{2} \varphi$.

[2]) See for instance WINKELMANN, loc. cit., p. 1134.

[3]) See for instance O. SCHLÖMILCH, Compendium der höheren Analysis, 3e Aufl. 1879, II, p. 322.

is the relation between the ordinate at the minimum z_0 of one of the curves and its width $2p$ [1]).

§ 7. Before proceeding to the discussion of the case $k < 0$ we shall first consider another problem, that of the ascension (or depression) of a liquid on the outside of a wide circular tube which is immersed in an infinitely extended liquid; the meridional curve then shows an infinitely extended branch RST (fig. 3) which may also be
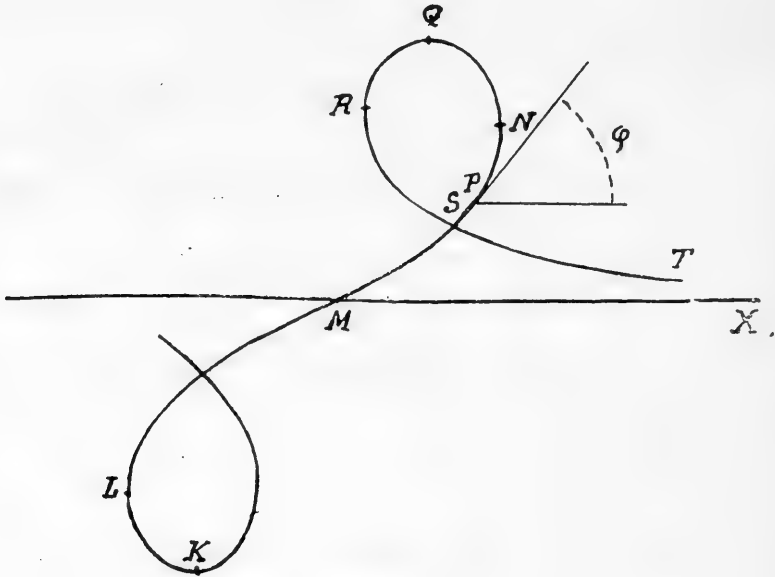

Fig. 3.

realised, in that case up to Q (cf. § 12), by lifting from the liquid a broad circular plate which is moistened by it.

The equation to this branch is found in a similar way to that of the branch $OEAB$ in fig. 1. We may again divide the curve into a marginal part whose abscissae measured from $x_Q = l$ are small with respect to l and a more distant part in which u becomes comparable to l and even large as compared to it, φ differing little from zero ($\varphi = 0$ at infinity).

In the same way as in §§ 2 and 3 (equation (2) is still valid) considering that $z = 0$ for $\varphi = 2\pi$ and $u = 0$ for $\varphi = \pi$ we find

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[1]) Putting $x_G - x_D = 2q$, this gives $p\sqrt{k} = q\sqrt{k} - 0{,}532$ (see § 3), and
$$z_0 \sqrt{k} = 1{,}842 \, e^{-q\sqrt{k}} \quad \ldots \ldots \ldots \quad (20')$$

$$\tfrac{1}{2} kz^2 = 2 \sin^2 \tfrac{1}{2} q - \frac{4}{3l\sqrt{k}}(1 + \cos^2 \tfrac{1}{2} \varphi) \ . \quad . \quad . \quad . \quad (21)$$

or

$$z\sqrt{k} = 2 \sin \tfrac{1}{2} q - \frac{1}{3l\sqrt{k}}(2 \cot an \tfrac{1}{4} \varphi - \sin q)^1), \ . \quad . \quad . \quad (22)$$

whence

$$u\sqrt{k} = \log \tan \tfrac{1}{4} \varphi + 2 \cos \tfrac{1}{2} \varphi - \frac{1}{3l\sqrt{k}}(\tfrac{3}{2} \log \tan \tfrac{1}{4} \varphi + \tfrac{1}{4} \cosec^2 \tfrac{1}{4} \varphi - \cos q - \tfrac{3}{2}). \ (23)$$

Putting φ successively equal to $\dfrac{\pi}{2}$, π and $\dfrac{3\pi}{2}$ the coördinates of N, Q and R are found as follows:

$$\varphi_N = \frac{\pi}{2} \qquad z_N\sqrt{k} = \sqrt{2} - \frac{1}{3l\sqrt{k}}(2\sqrt{2} + 1) = 1{,}414 - \frac{1{,}276}{l\sqrt{k}}$$
$$u_N\sqrt{k} = \{\log(\sqrt{2}-1) + \sqrt{2}\} - \frac{1}{6l\sqrt{k}}\{3\log(\sqrt{2}-1)+\sqrt{2}-1\}=0{,}532+\frac{0{,}372}{l\sqrt{k}} \qquad (24)$$

$$\varphi_Q = \pi \qquad z_Q\sqrt{k} = 2 - \frac{2}{3l\sqrt{k}} \qquad u_Q\sqrt{k} = 0 \ . \quad . \quad . \quad (25)$$

$$\varphi_R = \frac{3\pi}{2}, \qquad z_R\sqrt{k} = \sqrt{2} - \frac{1}{3l\sqrt{k}}(2\sqrt{2}-1)=1{,}414 - \frac{0{,}609}{l\sqrt{k}}$$
$$u_R\sqrt{k}=\log(\sqrt{2}+1)-\sqrt{2}-\frac{1}{6l\sqrt{k}}\{3\log(\sqrt{2}+1)-(\sqrt{2}+1)\}=-0{,}532+\frac{0{,}039}{l\sqrt{k}} \qquad (26)$$

§ 8. The outside portion of the curve RST, corresponding to values of φ, which differ but infinitely little from 2π and extending to infinity, is again determined by (9). Since, however, in this case z approaches zero at infinity, the solution will now be

$$z = aiH_0^{(1)}(iz\sqrt{k}). \ . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

where $H_0^{(1)}$ is HANKEL's function of order zero and of the first kind.

The integration-constant a is found by joining on to equations (22) and (23) putting $\varphi = 2\pi - \psi$, where ψ is infinitely small. In the same manner as in § 5 we then find

$$\log z\sqrt{k} = -u\sqrt{k} - 0{,}614 - \frac{u}{2l}, \ . \quad . \quad . \quad . \quad (28)$$

whereas for large values of x differing little from l equation (27) gives

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1) This is a known formula, except for a small reduction (cf. for instance WIN-KELMANN, loc. cit., p. 1148). See also A. FERGUSON, Phil. Mag., (6), 24, (1912) p. 837.

$$z = 2a \frac{e^{-x\sqrt{k}}}{\sqrt{2\pi x\sqrt{k}}} = \frac{2a}{\sqrt{2\pi}} \frac{e^{-l\sqrt{k}} \cdot e^{-u\sqrt{k}}}{\sqrt{l\sqrt{k}}} \left(1 - \tfrac{1}{2}\frac{u}{l}\right) \text{[1]}. \quad . \quad (29)$$

Therefore, putting $x_R = r$ and considering, that $r\sqrt{k} = l\sqrt{k}$ $+ u_R \sqrt{k}$ (eq. 26),

$$a\sqrt{k} = \tfrac{1}{2} \cdot 0{,}924 \sqrt{2\pi r\sqrt{k}} \, e^{r\sqrt{k}} \quad . \quad . \quad . \quad . \quad (30)$$

§ 9. According to (21) φ cannot become zero; on the other hand z can become zero at a point M (fig. 3) where φ goes through a smallest value. The continuation of the curve $QNSM$ to the left again consists of a series of elongated S-shaped curves, as represented diagrammatically in fig. 3 [2]).

The width of these curves is again small compared to l (abscissa of point M) and the following equation is found for them

$$kz^2 = 4\sin^2 \tfrac{1}{2}\varphi - \varphi_m{}^2 \pm \frac{8}{3l\sqrt{k}}(1 - \cos^3 \tfrac{1}{2}\varphi). \quad . \quad . \quad (31)$$

(the positive sign referring to the part, where $z > 0$, the negative sign to the rest); z becomes zero for

$$\varphi = \varphi_m = \frac{4\sqrt{n}}{\sqrt{3l\sqrt{k}}} \text{ or for } \varphi = 2\pi - \varphi_m, \quad . \quad . \quad . \quad (32)$$

according to whether the order n of the point M_n, where the n curve intersects the axis, is odd or even [3]).

Introducing a new angle ψ such that [4])

$$\sin \psi = \frac{\cos \tfrac{1}{2}\varphi}{\cos \tfrac{1}{2}\varphi_m} = \left(1 + \frac{2\sqrt{n}}{3l\sqrt{k}}\right)\cos \tfrac{1}{2}\varphi = \frac{1}{\lambda}\cos \tfrac{1}{2}\varphi, \quad . \quad (33)$$

we have in first approximation, as in the two-dimensional problem,

$$z\sqrt{k} = \pm 2\cos \psi \quad \pm u\sqrt{k} = \int_{\psi}^{\frac{\pi}{2}} \frac{d\psi}{\Delta\psi} - 2\int_{\psi}^{\frac{\pi}{2}} \Delta\psi \, d\psi, \quad . \quad (34)$$

u being measured from M. The total width $2p = x_Q - x_L$ is therefore given by the same expression as in § 6; hence

$$\varphi_m = 1{,}082 \, e^{-p\sqrt{k}}. \quad . \quad . \quad . \quad . \quad . \quad , \quad (35)$$

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[1]) NIELSEN, loc. cit.

[2]) Comp. WINKELMANN, loc. cit., p. 1138, fig. 400a.

[3]) In the first case the curve rises with increasing values of x, and φ changes from π to π through φ_m, in the other case the curve falls and φ changes from π to π through $2\pi - \varphi_m$.

[4]) Cf. WINKELMANN, loc. cit., p. 1137. We shall take ψ in such a direction, that $\psi = \pm \tfrac{1}{2}(\pi - \varphi) + \alpha$ (infinitely small), with $+$ for odd curves ($\varphi < \pi$), and $-$ for even curves ($\varphi > \pi$).

will be the relation between the width of the curve and the (sharp) angle at which it intersects the x-axis [1]).

§ 10. Capillary surfaces, whose meridional sections correspond to the curves DFG of fig. 2 or LMN (as also the one of opposite direction) of fig. 3 can be experimentally realized between two tubes the radii r_2 and r_1 of which differ comparatively little (say: $r_2 - r_1$ $< < l = \frac{1}{2}(r_2 + r_1)$), but still so much that $(r_2 - r_1) \sqrt{k}$ is a fairly high number. In general, however, for given values of $p = \frac{1}{2}(r_2 - r_1)$ and $l = \frac{1}{2}(r_2 + r_1)$, n will not be a whole number, i.e. the surface which establishes itself between two arbitrary tubes does not form part of those discussed in sections 6 and 9. Still, the equations as given remain valid, in other words the meridional curve is still represented by equations (14) or (31) and the capillary rise as well as the minimum angle are still given by equations (20') and (35').

The U-shaped or S-shaped curves, obtained in that way, again form part of a series of similar curves, but the first series does not now in general terminate on the side of the axis of revolution in a curve which runs approximately towards the origin, neither does the second series finish up on the side away from the axis in a branch running to infinity. It is easily seen, that the condition is as follows: the U-shaped curves become lower and lower on the side of the axis (towards the left) i.e. z_0 becomes smaller and after having gone through a minimum z_0 becomes imaginary, equation (14) assumes the form (3), that is: the U-shaped curves change into S-shaped ones. Conversely: the S-shaped curves assume towards the right smaller and smaller values of φ_m: ultimately φ_m becomes imaginary and the S-curves change into U-curves. [2])

§ 11. We shall now consider the case $k < 0$ (suspended drops).

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[1]) Putting $2q = x_N - x_L$, we find

$$\varphi_m = 1,842 \, e^{-q\sqrt{k}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (35')$$

[2]) If $(r_2 - r_1) \sqrt{k}$ is a moderate number, the results of the two-dimensional problem will be applicable as a first approximation without any simplification. If $(r_2 \cdot r_1) \sqrt{k}$ is very small, the section is circular in first approximation and the further approximation may be carried out in a way similar to that used in Suppl. N°. 42c for small drops.

If the difference $r_2 - r_1$ is not small compared to $l = \frac{1}{2}(r_2 - r_1)$, then in the neighbourhood of $x = r_1$, and $x = r_2$ the developments of sections 7 and 3 will hold, whereas in the intermediate region

$$z = ai \, H_0^{(1)} (ix \sqrt{k}) + b J_0 (ix \sqrt{k}), \quad . \quad . \quad . \quad . \quad . \quad (36)$$

the value of a being given by eq. (30) with $r = r_1$, that of b by h from equation (13) with $r = r_2$.

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Broad hanging drops cannot be obtained; it is clear that it is impossible to make drops hang from a wide tube, but also the drops which are formed on the under-side of a horizontal moistened plate do not attain large dimensions. If for instance a horizontal plate is immersed in water and then lifted out, the liquid which adheres to the plate collects in one or more drops which grow (sometimes flow together), drop off, grow again etc. but the width of the drops, finishing up tangentially to the plate, is in no way commensurate with the size of the plate.

The meridional section of the capillary surface in that case (as long as the drop is not yet constricted in the middle) consists of an undulating curve (fig. 4), the waves of which become lower and
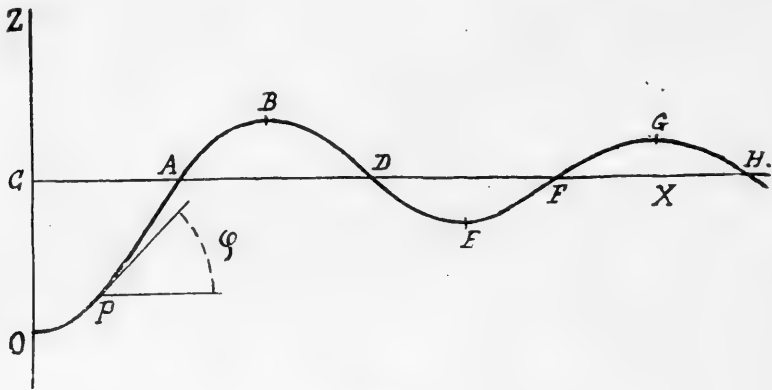

Fig. 4.

lower, as they are further away from the axis) [1]); the suspended drop represents the part OAB comprised between the axis and the first maximum. Curves drawn according to KELVIN's graphical method seem to show, that the distance of the successive maxima and minima from the axis of rotation increase with the radius of curvature at the top; however, there is a limit to this increase: even for very flat drops the distances remain moderate, as may be shown in the following manner.

When the drop is very flat, the angle φ may be considered as very small everywhere and the shape of the section is determined by (9), or putting $k = -k'$ by

$$z'' + \frac{z'}{x} + k'z = 0. \qquad \ldots \ldots \ldots \quad (9'')$$

This equation passes into (9′) by the substitution $x\sqrt{k'} = \xi$, $z = \eta$, therefore

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[1]) See WINKELMANN, loc. cit., p. 1146.

$$z = z_0 \, J_0 \, (x \sqrt{k}), \quad \ldots \ldots \ldots \quad (10')$$

z_0 being the ordinate $(-\, CO)$ at the top $\left(z_0 = \dfrac{2}{k'R_0} \right)$. As was to be expected, the course of this function corresponds to the curve of fig. 4 [1]). The maximum B is found at $x\sqrt{k} = 3.83$ [2]) and its ordinate is $z_B = 0.4028 \, z_0$, hence the total height of the drop is given by

$$H = 1,4028 \, z_0 = 1,4028 \times \frac{2}{k'R_0}, \quad \ldots \ldots \quad (37)$$

independently of the width (at least as long as R_0 is large).

At a large distance from the axis of rotation the curve approaches to

$$z = \frac{z_0}{\sqrt{\frac{1}{2}\pi x}} \, sin \, x \, \sqrt{k'} \quad {}^{3)} \quad \ldots \ldots \ldots \quad (38)$$

§ 12. Although the capillary constant has sometimes been calculated from observations on large drops (lying on a surface) or gas-bubbles and although methods are known which are based on that principle [4]), a really practical importance cannot be ascribed to them. It is only for the sake of completeness that we shall refer to these methods here in a few words and supplement them, where necessary.

In our discussion of the different ways in which surface-tension may be determined by means of very small drops and bubbles [5]), the methods were divided under three groups which might be called : the pressure-methods, the weight-methods, and the geometrical methods. In the methods of the first group the surface-tension σ is derived from the measurement of the pressure in a drop or bubble of given radius; in those of the second the force is measured which makes equilibrium with the surface-tension along a special line (in other words: the weight is measured of the liquid carried by the surface-

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[1]) See for instance JAHNKE und EMDE, Funktionentafeln.

[2]) For water (with $k = 13$) therefore $x_B = 1.06$ cm.

[3]) Cf. NIELSEN, loc. cit. For large values of x the general solution of (9″) is as follows

$$z = \frac{a}{\sqrt{\frac{1}{2}\pi x}} \, sin \, (x \, \sqrt{k'} + b). \quad \ldots \ldots \quad (38')$$

The other portions of the meridional curve, such as $BDEFG$ (fig. 4) do not seem to be possible. If a horizontal ring is moistened with liquid, one or more drops will remain suspended, but they do not unite into a ring of liquid.

[4]) See for instance WINKELMANN, p. 1155.

[5]) Leiden. Comm. Suppl. N⁰. 42d (1918); these Proc. XXI (1) p. 366.

tension) [1]); the third group contains the methods, in which σ is solely derived from the shape of drop or bubble (measurement of certain dimensions). This division is general and also holds for large drops and bubbles; only in that case the pressure-method is of no importance practically on account of the smallness of the pressures to be measured owing to the very slight curvature at the top; thus for instance equation (13) which gives the ascension at the axis of a wide tube of known radius is of no importance from a practical point of view.

Of greater importance in this case would seem to be the geometrical methods, which consist in measuring the coördinates of the points A and B of fig. 1, Q or R of fig. 3 and applying equations (6), (7), (25) or (26). But the application of these methods is hindered by the difficulty of an accurate measurement of the coördinates.

The greatest practical importance attaches to the weight-methods. GAY-LUSSAC already derived capillary constants from measurements of the force which is required to lift a horizontal disk, which is in contact with a widely extended liquid [2]), above the surface; this force, apart from the weight of the disk, is given by

$$P = \pi r^2 \mu\, gz - 2\pi\, r\sigma \sin \varphi, \quad . \quad . \quad . \quad . \quad . \quad (39)$$

where z is to be replaced by its value from (22) (with $l = r$). The simplest cases are those, where $\varphi = \dfrac{3\pi}{2}$ and $\varphi = \pi$ [3]); in the latter case, which can only be realized with a disk which is completely moistened by the liquid, the force is a maximum [4]).

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[1]) The method of measuring the capillary rise in narrow tubes belongs both to this and to the first group.

[2]) As mentioned by LAPLACE, Mécanique céleste, IV, 2e suppl. au livre **X**.

[3]) WINKELMANN, p. 1148 and 1156.

[4]) Accurately speaking this maximum is reached a moment before the disk is lifted to the greatest height (ordinate of Q, fig. 3); putting $\varphi = \pi + \varepsilon$, the maximum of P is reached, when $\varepsilon = \dfrac{4}{r\sqrt{k}}$. But as long as z is only known to a second approximation, this circumstance has no influence on the equation to be used in this case.

If there is an angle of contact i, both σ and i might be found from two observations, for instance one in which $\varphi = \dfrac{3\pi}{2}$ (this is impossible when $i > \dfrac{\pi}{2}$) and another in which the force is a maximum, in which case $\varphi = \pi + i$. If $i > \dfrac{\pi}{2}$, as for mercury, one might also determine the weight of a drop on a horizontal plate; in that case (39) is again applicable. Or the greatest force may be measured which is required to submerge a disk in a liquid (cf. A. MAYER, Sill. Journ., 4, (1897). p. 253.

Properly speaking, with the meaning given above to "weight-method", Gay-Lussac's method does not belong to this class, but is rather to be ranged under the 3rd group [1]). Proper weight-methods are those in which the capillary force is measured acting on a plate suspended vertically in a liquid [2]) or the force which is required to detach a thin horizontal ring from a liquid. The latter force, independently of the weight of the ring, is given by

$$P = 2\pi\sigma (r_1 \sin \varphi_1 - r_2 \sin \varphi_2) + \pi (r_2{}^2 - r_1{}^2) \mu gz, \quad . \quad . \quad (40)$$

r_1 and r_2 being the internal and external radii of the ring; the angles φ_1 and φ_2 for given values of z are determined by equations (4') and (22). The ring detaches itself, when z has become a little bigger than the ordinates of A (fig. 1) and D (fig. 3); putting

$$\varphi_1 = \frac{\pi}{2} + \varepsilon_1, \quad \varphi_2 = \frac{3\pi}{2} - \varepsilon_2, \quad \tfrac{1}{2}(r_2 + r_1) = r \quad \text{and} \quad r_2 - r_1 = \sigma,$$

P is found to be a maximum, when $\varepsilon_1 = \varepsilon_2 = \tfrac{1}{4}\sigma \sqrt{2k}$, whence

$$\frac{P_M}{4\pi\sigma r} = 1 + \tfrac{1}{2} \sigma \sqrt{2k} + \tfrac{1}{16} k\sigma^2 + \tfrac{1}{6} \frac{\sigma}{r} (2 \sqrt{2} - 1)^{[3]}) . \quad . \quad (41).$$

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[1]) According to (39) the force applied serves mainly (when $= \pi$, exclusively) to balance the hydrostatic pressure; the determination of the weight is therefore principally an indirect way of measuring the height z.

[2]) Wilhelmy's method. See Winkelmann. p. 1156.

[3]) This equation was found previously by others (cf. Winkelmann, loc. cit., p. 1157), all but the last term which, however, is of the same importance as the one preceding it.

The equation also holds in the case of a ring, which is forced down into a liquid like mercury.

Anatomy. — *"Comparison of the Brain Weight in Function of the Body Weight, between the Two Sexes."* By Prof. Eug. Dubois. (Communicated by Prof. H. Zwaardemaker).

The general relation of the brain weight in function of the body weight, between homoneuric species of Vertebrates could be accurately determined, because between them there often exist important differences in size. Thus it is known that their brain weight is proportional to the power 0.56 of their body weight, to $P^{0.56}$ (more accurately $P^{0.555..}$).

Between individuals of the same species and of the same sex, however, the brain weight of each is on an average proportional to a power of the body weight that has only half that value, but with the available data it could not yet be ascertained whether this is $P^{0.22}$, $P^{0.25}$ or $P^{0.28}$. The differences in the size of the body within a species are generally small, and when they become more considerable, as is the case with the Dog, we have to deal with such dissimilar material, that the relation in question can only be determined in approximation. For the human species we have, indeed, the advantage of having at our disposal a great number of determinations of weight, but here the brain weight has mostly been somewhat modified by the illness preceding death; in general it has somewhat diminished, but not to the same degree for all individuals. We may, indeed, make use of an indirect method of determining the brain weight, but it is clear that there are also objections to be alleged to this. There are as yet too few data available about normal individuals that have died a sudden death.

On the strength of the relations that appear to be valid between the cellular dimensions and volumes in the nervous system, I have become more and more inclined to consider $P^{0.28}$ (more accurately $P^{0.277..}$) as the correct interindividual factor, and to look upon my earlier attempts to interpret $P^{0.22}$ as superfluous. [1])

With regard to the determination of the intersexual exponent of relation the difficulties are, indeed, somewhat less, because it is

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[1]) These Proceedings. Vol. XVI (Meeting of December 27, 1913), p. 664—665.

possible to compute wider averages; but besides for Man there exist still few data. In 1907 Lapicque demonstrated[1]) that this exponent of relation, between the two sexes of the human species, is equal to that between homoneuric animal species of different weight. Among Europeans, man is on an average about 12 kilograms heavier than woman; his average brain weight is about one and a half hectograms more than that of woman. By taking the results of all the authors into account, Lapicque arrives at the round values 66 and 54 kilograms for the average body weights, and 1360 and 1220 grams for the average brain weights of European men and European women, to which an exponent of relation of 0.56 answers.

A much smaller exponent of relation holds within each sex; the brain weight varies much less considerably in comparison with the body weight. Lapicque draws attention to the discontinuity from one sex to the other, which thus appears. It had already been long observed that equal mean brain weights did not correspond to equal means of body height or of body weight of men on one side, and women on the other side; we have, in fact, to do here with two distinct series, like two species. The paradoxal character of this view, Lapicque continues, disappears when it is thus formulated: "dans le cas de dimorphisme sexuel la différence sexuelle doit être traitée au point de *vue mathématique* comme une différence spécifique"[2]). The difference in body weight between man and woman he justly considers as a clear secondary sexual property. In the brain weight there is now a difference of the same order, and assuming the above reasoning to be correct "ces deux caractères en réalité se ramèneraient à un seul, la différence de poids corporel; la différence de grandeur encéphalique ne serait qu'une conséquence harmonique"[3]).

On closer consideration I cannot concur with this last conclusion of the distinguished French physiologist. If it were correct, if actually one of the sexual properties in question were the necessary consequence of the other, we should find not only a mathematically equal relation, but also a *causally* equal relation between *all* dimorphous sexes as between the homoneuric species, for which

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[1]) Louis Lapicque, Différence sexuelle du poids encéphalique dans l'espèce humaine. Bulletins et Mémoires de la Société d'Anthropologie de Paris. Séance du 6 juin 1907. Paris 1908, p. 337—344.

[2]) Louis Lapicque, Comparaison du poids encéphalique entre les deux sexes de l'espèce humaine. Comptes rendus de la Société de Biologie de Paris. T. 63, Séance du 9 novembre 1907, p. 434.

[3]) Ibid., p. 746.

namely the brain weight and the body weight are in a fixed, causative ratio to each other. This is, however, not the case, as I propose to demonstrate [1]).

In order to trace the cause of the agreement found between the relation of Man and Woman and that of the homoneuric species, and at the same time of the departure from the inter-individual relation, it is required in the first place to examine whether this agreement and this deviation is *general*, and further *how* the sexual difference of the size of the body can have influence on the quantity of brain.

With regard to the first point LAPICQUE examined, already in 1907, whether for the common Rat (Mus norvegicus Erxl.) and the common Sparrow (Passer domesticus L.) the male sex possesses an excess of body weight and at the same time an excess of brain weight above the female sex, as in the human species [2]). He found this for both animal species, least clearly for the Rat. Of 15 full-grown male sparrows and 13 full-grown female sparrows the average body weights were 30.8 and 28.7 grams, and the average brain weights 994 and 959 milligrams, from which an exponent of relation of 0.5077 can be calculated [3]). Given however the slight differences of the average weights, which LAPICQUE himself (p. 747) calls only "approximatives", added to the comparatively great individual deviations, not much value should be assigned to this result. The body weight ranged for the male sparrows from 28.61 to 33 grams, for the female from 26.30 to 31.10 grams; the brain weight for the male sparrows ranged from 825 to 1080 milligrams, and for the female sparrows from 900 to 1110 milligrams! It is certainly not possible to conclude from this to a relation of the brain weight and the body weight between the two sexes of a similar nature as for Man; nor did LAPICQUE feel justified in doing so. For the rest it is well-known that the sexual difference in size for the Sparrow, if it does exist, is only met with to a very limited degree.

Sexual parity certainly applies to the Colin (Colinus virginianus L.), for which gallinaceous kind of bird HRDLICKA determined body weights and

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[1]) I have to rectify here my former erroneous assumption (These Proceedings, Vol. XVI, p. 659) that this relation would be the same in general for Vertebrates as for Man.

[2]) LOUIS LAPICQUE, Différence sexuelle dans le poids de l'encéphale chez les animaux: Rat et Moineau. Comptes rendus de la Société de Biologie. Tome 63 (1907), Séance du 21 décembre, p 746—748.

[3]) From the average weights of P and E in the two sexes repeatedly given there. On p. 748 the result of this calculation has been erroneously given as 0.57 there.

brain weights of 7 adult cocks and 9 adult hens[1]). The averages
are 124.1 grams for the body weight and 1.223 grams for the brain
weight of the cocks, and 123 grams for the body weight and 1.242
grams for the brain weight of the hens. From this we may conclude
to the equality of the two sexes in both respects.

An important sexual difference in body weight exists on the other
hand for the Domestic Hen. In what quantitative relation between
the two sexes is here the weight of the brain to that of the body?

Careful determinations of weight for an adult cock and an adult
hen made by FALCK[2]) and for an adult cock by WELCKER[3]) gave
the following results.

The body weight (without "ballast") of FALCK's cock, which was
extraordinarily large for its breed, was 1745,67 grams, the brain
weight 3.82 grams, the (net) body weight of the hen was 985.15,
and the brain weight 3.36 grams. From this we find an exponent
of relation 0.2248. By comparison of the same hen with WELCKER's
middle-sized cock, which had a "Reingewicht" (net weight) of 1445.7
grams and possessed 3.7 grams of brains, we obtain an exponent
of relation of 0.2513.

Given the comparatively much greater differences of the brain
weights between the two sexes, these results in themselves have
already a greater importance than those which LAPICQUE obtained
for the Sparrow. I found between an almost full-grown (more than
six months old) cock of the Leghorn breed, and an entirely full-
grown (two years old) hen of the same, but not quite pure breed,
the exponent of relation 0.4490 for (net) body weights of 1803 and
1197 grams (with emptied crop and stomach) and brain weights
of 3.75 and 3.12 grams. Seeing however, that this cock was not
fully grown, and was therefore too light for its brain weight, the
intersexual exponent of relation for the Gallus kind appears to be
half so great as for Man also here[4]).

This is in concordance with what we find for different species
of mammals. When in the series of MAX WEBER's dogs[5]) the 7

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[1]) A. HRDLICKA, Brain Weight in Vertebrates. Smithsonian Miscellaneous
Collections. Vol. 48. Publication N⁰. 1574 Washington 1905, p. 106.

[2]) C. PH. FALCK, Beiträge zur Kenntniss der Bildungs- und Wachsthumsge-
schichte der Thierkörper. Schriften der Gesellschaft zur Beförderung der gesammten
Naturwissenschaften zu Marburg. Band 8. Marburg 1857, p. 165–249, (p. 242).

[3]) R. WELCKER—A. BRANDT, Gewichtswerthe der Körperorgane bei dem Menschen
und den Thieren. Archiv für Anthropologie, Band 28. Braunschweig 1902, p. 53.

[4]) See below, p. 864.

[5]) MAX WEBER, Vorstudien über das Hirngewicht der Säugethiere. Festschrift
für CARL GEGENBAUR. Leipzig 1896, p. 111–112.

largest male dogs, which weigh from 12040 to 53000 grams, mean weight 27503 grams, and possess from 70 to 123, on an average 100 grams of brain, are compared with the 7 smallest female dogs, which weigh from 6000 to 14250 grams, mean weight 8908 grams, and possess from 64 to 86, on an average 77 grams of brain, we get an exponent of relation of 0.2318; i. e. very nearly the interindividual exponent for equal sexes of dogs, as determined by LAPICQUE.

Among RICHET's 157 dogs [1]) twenty are stated to be female. Possibly there are among the remaining dogs a *few* more female ones, not indicated as such; this does not make much difference for our purpose. When these twenty female dogs are compared with an equal number of male dogs, the bodyweights of which lie as close as possible to those of the female dogs, these weights for the two sexes together ranging from 5 to 37 kilograms, and the brain weights from 53 to 125 grams, we find (always comparing sets of ten):

between the largest ♂ and the smallest ♀ an exponent of relation 0.3287

,,	,,	,,	♂	,,	,,	,,	♂	,,	,,	,,	,,	0.3374
.,	,,	,,	♀	,,	,,	,,	♂	,,	,,	,,	,,	0.2988
,,	,,	,,	♀	,,	,,	,.	♀	,,	,,	,,	.,,	0.2899

It is evident that the discontinuity in the transition from the one sex to the other, which is so striking in the human species, does not exist here.

Of five domestic cats, examined by WILDER [2]), three male cats have a mean body weight of 3284 grams, and a brain weight of 29 grams, two female cats a mean body weight of 2410 grams and a brain weight of 27 grams, from which an exponent of relation of 0.2310 can be calculated.

According to LAPICQUE two bulls and six cows [3]), with mean body weights of 540 and 397 kilograms and mean brain weights of 480 and 429 grams, give 0.3650; two rams and three sheep, with body weights of 55 and 50 kilogr. and brain weights of 140 and 125 grams, give 0,2064 for the exponent of relation. Also the first mentioned

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[1]) CHARLES RICHET, Poids du cerveau, de la rate et du foie, chez les chiens de différentes tailles. Comptes rendus de la Société de Biologie de Paris, T. 3, 9me Série. Paris 1891, p. 405—415.

[2]) B. G. WILDER, Cerebral Variation in Domestic Dogs. Proceedings of the American Association for the Advancement of Science, 22nd Meeting (1873). Salem 1874, p. 238.

[3]) Bulletins et Mémoires de la Société d'Anthropologie de Paris. Séance du 6 juin 1907, p. 335—336.

value of the intersexual exponent of relation still lies much nearer 0.28 than 0.56.

Though the number of the individuals compared may be small, together these comparisons appear sufficient to prove that there exists another ratio of the brain weights to the body weights between the two sexes, very different from that in the human species.

For not a few, probably for by far the most species there does *not* exist sexual dimorphism in this respect, even where it might be expected from the external difference in the size, as for the Ox and the Domestic Hen. For those species which do not show sexual dimorphism in the size of their bodies this is still less to be expected in the brain weight. Of 16 male squirrels (Sciurus vulgaris L.) I found the body weight on an average 331 grams, and of 15 female squirrels killed in the same neighbourhood on an average 326 grams. Thus much may already be inferred from the not yet numerous determinations of the brain weight, that for this species the greater exponent of relation between the sexes does certainly *not* hold.

For the human species, on the contrary, the important internal dimorphism of the brain weight, which finds its expression in the exponent of relation of double the value for other species, corresponds to the striking external sexual dimorphism of the body weight; in ratio to the body weight man has a disproportionally greater amount of brain than woman.

Of great consequence is the fact that a javanese monkey species, the Budeng, *Semnopithecus maurus* F. Cuv. (incl. *pyrrhus* Horsf.), entirely agrees with the human species in this respect, as follows from the body weights and brain weights, according to determinations by KOHLBRUGGE [1]) of a number of male and female animals killed in the state of nature. I mentioned this conformity in a few words already in 1913 [2]). This sexual dimorphism in the quantity of brain, of the same nature and to the same extent as for Man is most likely a general characteristic of the Monkeys, at least for those of the Old World, for they show universally considerable sexual differences in size of the body and at the same time a certain sexual difference in the requirements of the mode of life, which in Man are attended with the dimorphism of the quantity of the brain.

From the values of P and E determined by KOHLBRUGGE for the species mentioned, those which may serve for the calculation of an

[1]) J. H. F. KOHLBRUGGE, Mittheilungen über die Länge und Schwere einiger Organe bei Primaten. Zeitschrift für Morphologie und Anthropologie, Bd. II. Stuttgart 1900, p. 54.

[2]) These Proceedings, Vol. XVI, p. 659.

intersexual exponent, are fully recorded in Table I, so as also to show the individual values of the body weight and the brain weight by the side of the mean values.

TABLE I. — Body weight and brain weight of *Semnopithecus maurus* F. Cuv.
  · (Determinations in Java by J. H. F. KOHLBRUGGE)

6 adult ♂			12 adult ♀			4 adult or nearly adult (*) ♂ E, in grams	7 adult or nearly adult (*) ♀ E, in grams
N⁰.	Length from nozzle to anus, in cm.	P, in grams	N⁰.	Length from nozzle to anus, in cm.	P, in grams		
18	66	16500	3	65	12500	81.7*	76
13	68 .	10000	6	64	12000	81	76*
16	64	8750	29	—	7500	78	73*
14	67	8100	4	64	6970	71	68
17	64	7500	5	64	6900		66
15	65	7000	32	64	6900		66†
			1	67	6800		57.5
			2	66	6500		
			7	64	6240		
			30	61	6100		
			31	64	6000		
			—	61 †	6100†		
Av.	65.7	9642	Av.	64	7542.5	Av. 77.93	Av. 68.93

I have omitted a single particularly low body weight, 3600 grams for a female specimen (KOHLBRUGGE's N⁰. 11), because I could not place a corresponding low body weight of a male specimen over against it. The curves of variation are now for the two sexes, one-sided towards the same side, and may, therefore, be compared. On the other hand in this and in the following table another (unnumbered) female specimen (†) has been inserted, which is not met with among KOHLBRUGGE's records, of which the latter had kindly furnished the data to me on the day of the determination (in 1897). Among the data also three determinations of brain weights have been inserted of almost adult individuals (in the second period of teething), because

these brains may certainly be considered as having reached their full ponderal development. [1])

Now the following result is obtained:

$$(log\ 77.93 - log\ 68.93) : (log\ 9642 - log\ 7542.5) = 0.5006$$

By comparison of the averages of the corresponding weights of the body and the brain individually, of three adult male with those of four adult female budengs, recorded in Table II, an exponent of relation **0.5248** is found.

TABLE II. — Body weight and brain weight of *Semnopithecus maurus* F. Cuv.
(Grams)

3 adult ♂			4 adult ♀		
	P	E		P	E
Nº. 18	16500	78	Nº. 3	12500	76
„ 14	8100	81	„ 4	6970	57.5
„ 15	7000	71	„ 5	6900	68
			—·	6100	66
Av.	10533	76.7	Av.	8117.5	66.9

It follows that for this monkey species between the sexes an entirely different law for the ratio of the brain weight to the body weight is valid than for the other discussed animal species, i.e. the same as holds for the human species.

Evidently this deviation with respect to so many other animal species does not only rest on the difference of size between the sexes, for then it should be much more frequently found, among others also for the Ox and the Domestic Hen. This quantitative difference in body weight must be accompanied by some other difference, and this must necessarily be a *qualitative* difference, in contrast also with two homoneuric species, the body weights of which are only different as far as the quantity is concerned.

As genuine secondary sexual characteristics of a qualitative nature the following are well-known. In all the races of Mankind woman

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[1]) J. H. F. KOHLBRUGGE, l.c., p. 48: "Bei Semnopithecus erreicht das Gehirn so frühzeitig sein Maximalgewicht dass es schon bei Säuglingen dem erwachsener Thiere ganz nahe steht".

has a comparatively longer trunk and shorter limbs, broader hips, narrower shoulders, internally a disproportionally more slenderly built skeleton, and less powerful muscles, on the other hand a more fully developed layer of fat in the skin, which rounds off the forms. Thus equal quantities of weight do not mean the same thing in the two sexes. Especially the muscles constitute a smaller part of the body weight for woman, the smaller because the arms and legs, to which for both sexes the four fifth part of the entire muscle weight belongs (for man even slightly more), are also shorter for woman.

With the smaller percentage of muscle weight of the female body must necessarily be in connection a disproportionally slighter quantity of the nervous system *with regard to the body weight.* The main point is, therefore, to examine whether the small quantity of brain in proportion to the body weight for the human female sex, in comparison with other female Mammals, corresponds to the disproportionally slighter muscularity.

This appears to be actually the case; *in proportion to the weight of the muscles* the ratio of the brain weight between the two sexes of the human species is the same as between the two sexes of any other animal species and between individuals of the same sex. The sexual dimorphism of the brain weight of Man and certainly of many if not all the Monkeys exists only in relation to the body weight. For most animal species, whether or no they are externally sexually dimorphous, cerebral dimorphism is lacking, also in comparison with the body weight, probably even for Pinnipeds, though of some species of this order the males are on an average three or four times heavier than the females.

The best data that we have at our disposal concerning the muscularity of the male and the female body, were furnished by FRIEDRICH WILHELM THEILE and HERMANN WELCKER, published only after their deaths, of the latter by A. BRANDT[1]), of the former by W. HIS[2]).

Through his determinations of the weight of the separate muscles of a considerable number of corpses of adult men and women and children, carried out with scrupulous accuracy, THEILE has raised to himself a lasting memorial. For our purpose

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[1]) WELCKER—BRANDT, l.c., p. 38—40.

[2]) F. W. THEILE, Gewichtsbestimmungen zur Entwickelung des Muskelsystems und des Skelettes beim Menschen. Nova Acta der Ksl. Leop.-Carol.-Deutschen Akademie der Naturforscher. Band 46, N⁰. 3, Halle 1884, p. 133—471.

it detracts somewhat from their value that mostly the body weights of the adult men and women were not determined. These weights are not wanting in the tables of WELCKER.

In Table III I have recorded all WELCKER's data for so far as they refer to the muscle weight, except woman N°. 3. The determinations put together by WELCKER concern mostly men and women in good health, who have died a sudden death. Except I. 5 and III. 4, which have been borrowed from BISCHOFF's "Hirngewicht des Menschen", they were carried out by him and other investigators,

TABLE III. — Body weight and muscle weight of 10 men and 3 women.
(Borrowed from Tables I to III, p. 38 to 40, in WELCKER-BRANDT, Gewichtswerthe der Körperorgane bei dem Menschen und den Thieren)

	N°.	Age, in years	Height, in cm.	Body weight, P, in grams	Muscle weight, M, in grams	Relative weight of the muscles in % of P
Men	I. 1	—	157	46870	21451	45.77
	„ 2	probably under 50	165	53714	25156	46.83
	„ 3	ca. 26	184	61267	26563	43.35
	„ 4	50	176	65050	28017	43.07
	„ 5	33	168	69668	29102	41.77
	II. 1	36	163	50500	18484	36.60
	„ 2	—	163	54000	16625	30.79 P relatively high by dropsy
	„ 3	—	168	56330	23467	41.66
	„ 4	—	172	61500	25594	41.62
	„ 5	42	172	65250	30574	46.86
	Averages	—	168.8	58415	24503	41.95
Women	III. 1	61	153	44000	14776	33.58
	„ 2	55	160	47000	15625	33.24
	„ 4 [1]	22	159	55400	19846	35.82
	Averages	—	157.3	44800	16749	34.32

[1] Woman N°. 3 has been omitted here: "Diese Bestimmungen" (namely one more of a newly born child) "falls sie sich überhaupt auf normale Körper beziehen, schliessen erhebliche Fehler in sich". (loc. cit , p. 14).

and they were either not made known elsewhere or in places that are no longer accessible.

In this table the body weights are mostly small for the body heights, which will probably be owing to the fact that most examined men and women did not possess a normal weight at the time of their death. According to this and the following table the *relative* weight of the muscles in each sex is, however, barring exceptions, a little variable property, even in more advanced age. Nothing else is, indeed, to be expected from so prominent a system of organs as that of the muscles, which as regards quantity, participates for about a third of the weight in the composition of the body, and the development of which is in close connection with that of other important parts of the bulk of the body, as the skeleton and many others.

The sexual difference in the relative weight of the muscles assumes the greater importance in consequence of their preponderant influence on the bulk of the body. This difference is very considerable. In ratio to the same body weight men are no less than over **22** $\%$ more muscular than women according to the averages in Table III.

It is very much to be regretted that in THEILE's for the rest very careful determinations of weight of the muscles, from which I composed Table IV, the body weight could be stated in but a single case. THEILE himself calculates the average relative muscle weights by simply assuming, according to the general values given by QUETELET, the average body weight to be 68 kilograms for his 8 vigorous men, suicides or having died of an acute illness, and the average body weight to be 54 kilograms for his 4 vigorous women, who had died of an acute illness; he then finds (p. 223): "Die Gesamtmuskulatur des erwachsenen kräftigen Weibes scheint also durchschnittlich noch nicht ein Drittel des Körpergewichts zu erreichen, während sie beim erwachsenen kräftigen Manne durchschnittlich mehr als ein Drittel des Körpergewichts beträgt". It appears possible to approximate the real weights still somewhat more closely by taking into consideration the individual heights and what is further noted about every individual, for the estimation of the weights. The number of the determinations serviceable for my purpose is then confined to 4 men and 4 women. THEILE's man N° 8 has not been inserted in Table IV on account of his, in comparison with the other men and women, high age of 54 years. Estimating his weight, with a height of 160.2 cm., at 57 kilograms, he is found to have a relative muscle weight of 38 $\%$.

As appears from the average heights the men are below the average computed from very large numbers, the women above the large-number average. Beyond doubt THEILE thus overrated the body weight of the former, but on the other hand underrated that of the women; in his time there were not yet so many data about the correspondence of body weight and height available in the literature as there are at present.

In Table IV the average relative muscle weight of the women has been calculated somewhat too low, as in two cases the total muscle weight was put as double that of the *lefthand* side, without

TABLE IV. — Body weight and weight of the muscles of 4 men and 4 women (According to determinations by F. W. THEILE. The body weights, except of N⁰. 3, estimated by me)

Sex	N⁰.	Age in years	Height, in cm.	Body weight, P, in grams	Muscle weight, M, in grams			Relative muscle weight, in $\%$ of P	
					Right	Left	Total		
Men	1	24	167.2	62000	12033.8	11866.5	23900.3	38.55	
	2	24 à 26	167.2	66000	12825.4	12735.0	25560.4	38.73	"mit strotzend voller Muskulatur" P directly determined
	3	26	165.1	64000	14608.0	14308.2	28916.2	45.19	
	5	35	162.4	59000	10718.0	estimated	21300.0	36.10	
	Averages	—	165.5	62750	12546.3	12372.9	24919.2	39.64	
Women	13	22	162.4	62000	—	9261.6	calculated as	29.88	extraordinarily stout
	14	22	148.9	50000	—	7388.1	double the	29.55	vigorous body
	15	35	161.1	56000	—	8041.5	determined half	28.72	"mässig entwickelte Muskulatur"
	16	44	163.3	62000	9549.3	—	of the body	30.80	"stark knochig" "kräftige Muskul."
	Averages	—	158.9	57500	—	—	—	29.74	

being balanced by other cases, in which the *righthand* side was doubled. When on account of this the relative muscle weight is put at **30 %,** this will, indeed, be very near the real average of the examined women, if their body weights have been correctly estimated. The average relative muscle weight of the men must, on the other hand, be considered as slightly too high, one of the men being extraordinarily muscular. On account of this the average relative weight of the muscles of the men, for so far as it is possible to approximate it in such an estimation of the body weights, may be put at **38 %,**

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which per unity of body weight is almost **27 °/。** more than that of the women.

Apart from a few exceptions the relative weights of the muscles according to the data of THEILE are lower than those according to the data of WELCKER. This is partly owing to the circumstance that the body weights given by WELCKER are in general low for the body heights, but probably to a greater extent to another circumstance. WELCKER'S muscle weights, with the exception of II. 1 and II. 5, were, namely, determined *indirectly*, with a certain necessary additional weight on account of the loss of the weights of the other organs, which have been subtracted from the body weight; THEILE, on the other hand determined *directly* the singular muscle weights, in which laborious manipulations some loss of weight, at least through evaporation, is inevitable.

These deviations, however, applying equally to both sexes, the *ratio* between them is certainly but little changed by this difference of the methods. WELCKER's man III. 5 must have been an exceptionally powerful individual, indeed, just as THEILE's N°. 3, but the high value of III. 5 is balanced by the low values of II. 1 and II. 2.

Hence • Man is *twenty-two per cent* according to one, *twenty-seven per cent* according to the other series of determinations per unity of body weight more muscular than Woman. That these results, even apart from the uncertainty of the estimations in question, founded as they are on a small number of observations, may still depart somewhat from the general average, notwithstanding the prevailing constancy of the relative muscle weight within each sex, needs no further demonstration.

Nor has perfect certainty been attained as regards the average body weights of European men and women. But when with LAPICQUE the averages are put at 66 and 54 kilograms, it is found that these values are precisely in the same ratio to each other as the average relative muscle weights according to THEILE's determinations. In fact $\frac{66}{54}$ is $= 1,2222$ and $\frac{41.95}{34.32}$ is $= 1.2223$.

If then the male body per unity of weight, has 22°/。 more muscle weight than the female body, the weight of the former is, besides, absolutely greater than the latter in the same ratio.

In his excellent handbook on anthropology [1]) RUDOLF MARTIN assumes as the average weight of European woman 52 kilograms,

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[1]) R. MARTIN, Lehrbuch der Anthropologie in systematischer Darstellung. Jena 1914, p. 237.

and of European man 65 kilograms, i.e. 25°/₀ more. This ratio comes nearer that of the average relative muscle weights, computed from the data of THEILE.

Hence it may safely be assumed that for the human species, the male body has higher relative weight of the muscles than the female body in the same geometrical ratio as the former has already more weight than the latter. In other words: *Between Woman and Man the absolute weight of the muscles varies in rate of the square of the body weight.*

This now accounts for the fact that between Woman and Man the brain weight, in function of the body weight, increases proportionally with the square of the increase of the brain weight, in function of the body weight, between the two sexes of most other species, namely, proportionally to $P^{0.56}$ between Woman and Man, and proportionally to $P^{0.28}$ between the two sexes of most animal species.

When the exponent of relation of the brain weight between **Woman** and **Man** is really not calculated with respect to the average body weight, but with respect to the absolute average *muscle weight*, it is found to be equal to the exponent of relation of the brain weight in function of the body weight, between individuals of identical species, viz. about **0.28**, instead of **0.56**.

There are only few direct data about the ratio of the muscle weights between individuals of one sex of identical species, between the two sexes and between different homoneuric species at our disposal. From WELCKER's and THEILE's determinations of the muscle weights for the human species it is already clear that these weights, between individuals of identical sex, vary proportionally to the body weight.

We find the same proportionality in other species of Vertebrates. Of two almost adult dachshunds from the same litter, examined by FALCK[1]), the somewhat older and heavier female had slightly higher relative muscle weight (which rapidly increases with the age in both sexes) than the male. Though the full-grown male of the albino rat (Mus norvegicus Erxl.) weighs on an average about 300 grams as against the female about 200 grams, they are equally muscular, judging from JACKSON and LOWREY's determinations[2]) on not yet full-grown animals. Comparing six males of 150 days, with an

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[1]) C. PH. FALCK, Beiträge zur Kenntniss der Wachsthumsgeschichte des Thierkörpers. Archiv für pathologische Anatomie und Physiologie (VIRCHOW), Band VII. Berlin 1854, d. 37 – 75.

[2]) H. H. DONALDSON, The Rat. Philadelphia 1915, p. 76.

average weight of 218.7 grams, of which **93.38** grams of muscle weight, with seven females of the same age, with an average weight of 154.8 grams and a muscle weight of 65.94 grams, we find a relative weight of the muscles of 42.7 $^0/_0$ for the males and 42.6 $^0/_0$ for the females. For four male albino rats (Mus norvegicus Erxl.), of 365 days, weighing on an average 260.2 grams, the mean relative weight of the muscles was 46.5 $^0/_0$, and two female albino rats, weighing on an average 183.5 grams, had a mean relative muscle weight of 43.3 $^0/_0$. Calculated with the absolute muscle weights 761.8 and 517.1 grams [1]) given by WELCKER there was equality of relative muscle weight (viz. 52.7 and 52.5 $^0/_0$) between the cock of 1445.7 grams and the hen of 985.1 grams of body weight. For the above mentioned almost full-grown Leghorn cock I found 213.9 grams or 11.9 $^0/_0$ of the body weight for the joint weight of the three left-hand and the three righthand pectoral muscles; for the fullgrown hen 174.6 grams or 14.6 $^0/_0$ of the body weight! In about the same geometrical ratio the muscles of the shank of the hen exceeded those of the cock. Evidently the cock was less muscular, because it was not quite full-grown. When the body weight of the cock is calculated with equal relative muscle weight as the hen, the exponent of relation becomes 0.2984. An adult male and an adult female lizard (Lacerta agilis L.) according to WELCKER [2]) have almost the same relative muscle weight; so have a male and a female Spotted Land-salamander (Salamandra maculosa Laur.) according to his data.

But such a proportionality of body weight and muscle weight, between individuals of identical species and equal sex, as well as between the two sexes, may certainly be assumed, if this proportionality also exists between different homoneuric *species*.

Very valuable data about this matter are furnished by A. MAGNAN [3]). From the values which he gives for the average relative weights of the musculus coraco-brachialis (which muscle raises the wing) in different orders of Birds, taken in general (p. 126), proportionality with the body weight already appears. But it seems to me to be of importance to examine this within every order and also for the

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[1]) WELCKER—BRANDT, loc. cit., p. 53. — FALCK's muscle weight corrected by WELCKER. Among these muscle weights for the cock and the hen also a certain part of the skeleton is included.

[2]) Loc. cit., p. 55.

[3]) A. MAGNAN, Relation chez les Oiseaux entre le poids de leurs muscles pectoraux et leur manière de voler. Bulletin du Muséum national d'Histoire naturelle. Année 1913, N°. 1, Paris 1913, p. 40—52. Les muscles releveurs de l'aile chez les Oiseaux. Ibid., N°. 2, p. 126—128.

musculus pectoralis major, which is from 5 to 10 times more bulky than the coraco-brachialis. By pressing the wing down, this powerful muscle acts more directly in the locomotion, and is quantitatively very differently developed in the different orders according to their mode of flying, most so for the Gallinae and the Columbidae, which fly rowing '(vol ramé), least for the Birds of Prey and the Owls, which mostly fly floatingly (vol plané), little too for the Marine Palmipeds, which sail through the air in their flight (vol à voile). In connection with this the area of the wing and the volume (or weight) of the principal muscle active in flying, the musculus pectoralis major are in reversed ratio to each other. To mention only the extremes, the Birds of Prey have on an average double the wing surface of the Gallinae, and their musculus pectoralis major has only half the weight. For our purpose it is, however, necessary to know whether also under for the rest equal circumstances, the weight of the latter muscle is proportional to the body weight. If this appears to be actually the case, we may safely conclude that it holds for the whole of the muscles and for other Vertebrates too. Hence we should only compare Birds of the same order, which also resemble each other as much as possible in form and mode of flying, because on account of the presence of two counteracting factors, area of the wing and development of the muscle, deviations of the former, also within a same order, immediately assume great importance for the latter. From MAGNAN's determinations I have chosen 10 pairs, formed from 20 species of Birds, each pair consisting of two species which, though different in size, resemble each other as closely as possible, as regards form of the body and flight, and calculated the relative body weight (P), the relative weight of the musculus pectoralis major (Mp), the relative surface of the body $(S,$ as $P^2/_3)$, and the relative area of the wing (A) [1]), and for (mostly other individuals of) the same species also the relative weight of the musculus coraco-brachialis (Mc).

When specific and individual deviations are disregarded, there thus appears to exist a simple proportionality of the weight of the muscles with the weight of the body. In the average values found the weight of both muscles is slightly more than proportional to the body weight; but most probably this is chiefly to be attributed to the circumstance that also the area of the wings becomes on an average somewhat larger in proportion to the surface of the body; which

[1]) A. MAGNAN, Variations de la surface alaire chez les Oiseaux, l.c , Année 1913, N⁰. 2, p. 119—125.

TABLE V. — Relative weights of the body (*P*), the musculus pectoralis major (*Mp*) and the musculus coracobrachialis (*Mc*), and relative surfaces of the body (*S*) and the area of the wings (*A*) in 10 pairs, formed from 20 species of Birds. (Calculated from the determinations of A. MAGNAN)

	P	Mp	$\dfrac{S}{(P^2/_3)}$	A	P	Mc
1. Buzzard (Buteo vulgaris Leach) — Kestrel (Tinnunculus alaudarius Gm.)	4.715	4.812	2.812	3.235	5.862	4.568
2. Black-backed Gull (Larus marinus L.) — Black-headed Gull (Larus ridibundus L.)	8.025	9.115	4.008	3.158	7.285	8.781
3. Silvery Gull (Larus argentatus Brunn.) — Tern (Sterna hirundo L.)	6.566	6.471	3.506	3.470	6.860	6.760
4. Hooded Crow (Corvus cornix L.) — Jay (Garrulus glandularius L.)	3.140	3.434	2.144	2.332	3.102	3.062
5. Blackbird (Turdus merula L.) — Hedge Sparrow (Accentor modularis L.)	4.117	4.143	2.569	2.583	4.601	4.052
6. Brant Goose (Bernicla branta Briss.) — White-eyed Poachard (Fuligula nyroca Guld.)	2.246	2.196	1.715	2.258	2.246	1.705
7. Wild Duck (Anas boschas L.) — Winter Teal (Querquedula crecca L.)	3.174	2.555	2.160	2.025	3.041	2.200
8. Golden Plover (Charadrius pluvialis L.) Ringed Sand-plover (Charadrius hiaticula L.)	3.554	4.443	2.329	2.470	3.554	4.875
9. Russet Godwit (Limosa Baueri Naum.) — Marsh Green-shank (Totanus stagnatilis Bechst.)	3.694	3.590	2.390	2.342	3.694	4.697
10. Rock Pigeon (Columba livia Briss.) — Turtle Dove (Turtur auritus Ray)	3.592	4.126	2.346	2.570	3.649	3.657
Averages	4.2823	4.4885	2.5979	2.6443	4.3894	4.4357

seems also required to keep the body, which becomes disproportionally heavier with regard to its surface, floating.

Thus through this research the necessary certainty has been obtained that between homoneuric species, under for the rest equal circumstances, the weight of the muscles varies proportionally with the body weight. If this holds between large and small homoneuric *species*, it may be assumed a fortiori that the *individuals* of a same species and of equal, generally also of different sexes, certainly possess no greater relative muscle weight than the smaller individuals, because between them the brain weight, in function of the body weight, varies much less than between homoneuric species.

For man, however, in comparison with woman, the absolute average weights of the muscles increase as the square of their average body weights. Together with this also the brain weight, in function of the body weight, as the square of the increase of the brain weight, in function of the body weight, between individuals of identical species, mostly even of different sexes. For man, compared with

woman, therefore, as $P^{0.28} \times P^{0.28}$ or $P^{0.56}$, just as between homo-neuric species.

In function of the muscle weight, however, the brain weight in every species — also in the human species — between individuals of equal and of different sexes, varies proportionally to $M^{0.28}$.

This is different between homoneuric species. For them the brain weight varies both proportionally to $M^{0.56}$ and to $P^{0.56}$; *in proportion to the weight or volume of the muscles* the brain weight increases, therefore, more than within a species.

Here an important difference in the relation between homoneuric species and between the two sexes — also in the human species — becomes apparent, with which without doubt differences in the anatomical and physiological relation of the nervous system and the muscular system are connected.

In fact it has already long been known that the muscle fibers of man are on an average considerably thicker than those of woman. Bowman [1]) found (already in 1840) that the mean diameter for man is about a fourth larger, corresponding to a ratio of the area of the sections of 1.664. Schwalbe and Mayeda [2]) lay great stress on the "bedeutenden Einfluss", which the sex has on the thickness of homologous muscle fibers. "Ganz algemein liegen in den hier verwerthbaren Messungen die Kaliber-Maxima im weiblichen Muskel tiefer als im männlichen" (p. 502). The same sexual difference holds for the average calibers of the comparable measurements, represented in Table VI. So also for the relative widths and maxima of the "curves of variation", from which appears perfect uniformity of these mean curves (for the width as well as for the maxima the ratio is 1.653); which in connection with the functional relation between the nerve and the muscle found by Keith Lucas, Mines, and by Lapicque in their researches, is of great importance. [)]

The average area of *section* of the fibers of these three muscles

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[1]) W. Bowman, On the Minute Structure and Movements of Voluntary Muscle. Philosophical Transactions of the Royal Society of London for the year 1840. Part II, London 1840, p. 461.

[2]) G. Schwalbe und R. Mayeda, Ueber die Kaliberverhältnisse der querge-streiften Muskelfasern des Menschen. Zeitschrift für Biologie (Kühne und Voit). Band 27, München und Leipzig 1890, p. 482—516.

[3]) K. Lucas, in Journal of Physiology. Cambridge 1905, p. 125; 1909, p. 113. — G. R. Mines, Ibid. 1913, p. 1. — L. Lapicque, in Comptes rendus de la Société de Biologie. Paris 1913, p. 35. — The fibers of a skeleton muscle can, namely, each of them separately get into contraction. Without doubt this must be in con-nection both with the thickness of the muscle fibers and with the thickness of the nerve fibers.

TABLE VI. — Diameter of the muscle fibers. (From measurements by G. SCHWALBE and R. MAYEDA)

| | Mean diameter (in micra) | | Relative width and maximum of the curves of variation | |
	Man	Woman	Man	Woman
Biceps brachii	51.7	39.5	14 20	12 17
Sartorius	51.8	36.2	18 24	13 17
Gastrocnemius	57.5	47.5	22 28	17 22
Averages	**53.7**	**41.1**	18 24	14 18.7

is **1.708** times larger for man than for woman; of both sexes "kräftige Leichen" were compared. In the "muskelkräftige" men and women of THEILE the homonymous muscles had the weights indicated in Table VII.

TABLE VII. — Muscle weights (in grams). (From determinations by F. W. THEILE)

| | Four men | | | | | Four women | | | | |
	n^0. 1(r)	2(l)	3(l)	7(r)	Mean	n^0. 13(r)	14(l)	15(l)	16(r)	Mean
Biceps brachii	179.2	152.9	181.7	196.3	177.5	96.9	72.1	77.8	104.0	87.7
Sartorius	143.5	211.8	201.0	207.5	191.0	110.6	73.9	102.5	100.6	96.9
Gastrocnemius	346.0	291.4	449.2	460.7	386.8	259.1	223.7	238.6	252.2	243.4
Averages	222.9	218.7	277.3	288.2	**251.8**	155.5	123.2	139.6	152.3	**142.7**

The average weight of the three muscles is 1.765 times greater for the men than for the women. When it is assumed that in proportion to the greater bodily lengths, the muscles were on an average 1.069 times longer for the men [1]), we find the area of section on an average **1.651** times larger than for the women. This latter value comes very near the value 1.708 found for the increase of the average area of

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[1]) Of the man N^0. 5 the gastrocnemius had not been weighed separately. I chose for this N^0. 7, "Mann von mehr als mittlerer Grösse", for whose height I assumed 175 cm. The average height of these four men then becomes 168.6 cm.; the average height of the four women is 158.9 cm. The ratio of the lengths of the limbs of these men to those of these women may thus be put at about 170 : 159 = 1.069.

section of the muscle fibers. As with the length of the muscle in general also varies the length of its fibers [1]), and accordingly the average number of them remains the same, it may be assumed that *the average number of the muscle fibers of man is the same as that of woman.* This is then also valid for the number of the motor nerve fibers, and also of all other nerve fibers and of the neurones.

Thus the ratio of the brain weights can only be determined by the length and the area of section of the nerve fibers, or one of them (not by the number). The volume of the cell-bodies is minute in comparison with that of the other components of the neurones. Now the brain weights are to each other in the same ratio as the length of the nerve fibers, from which follows that the area of section of the nerve fibers remains the same, just as between individuals of equal sex of a species. Between homoneuric species, on the other hand, the area of section of the nerve fibers varies proportionally to $P^{0.28}$.

Hence there is no difference in the sexes as regards the physiological relation between the muscular system and the nervous system. For the human species, however, and certainly also for many, if not for all Monkeys, the male sex does agree with the males of other species, but the female sex does not, as far as relation between these two systems of organs and the bulk of the body is concerned. Dynamically, woman, in as much as she has to move a disproportionally greater body weight for her strength, is inferior to man. The ratio of the body weights is regulated here so, as woman possesses disproportionally less muscle, that the dynamic disadvantage of the large individuals as against the small ones, is cancelled for man as against woman, which requires squaring of the common ratio of the brain weight and the muscle weight to the body weight.

Thus it is not only for the human species, but also for other Primates. The peculiarity existing here: slighter mobility of woman, and on the other hand great mobility of man can only be accounted for by the very special and contrary mechanic requirements which, in this order, maternal care imposes on one, and family life on the other sex. It is needless to point out the significance which this has also in a sociological respect, and to demonstrate the impossibility that we shall ever be justified in saying: "nous avons changé tout cela".

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[1]) Cf.: R. MAYEDA, Ueber die Kaliberverhältnisse der quergestreiften Muskelfasern. Zeitschrift für Biologie (KÜHNE und VOIT), Band 27. (1890), p. 142 and 146.

Astronomy. — *"The Distribution of the Absolute Magnitudes among the Stars in and about the Milky Way"*. (Second Communication). By Dr. W. J. A. SCHOUTEN. (Communicated by Prof. J. C. KAPTEYN).

In a former communication we have communicated the results of a research in which we determined according to KAPTEYN's method the mean luminosity curve for the whole sky and the corresponding curves for zones of different galactic latitude. We intend to communicate in this essay the results that were found by treating the same data according a method first proposed and used by SCHWARZSCHILD.

1. SCHWARZSCHILD's *method and his results.*

SCHWARZSCHILD starts from the integral formulae that were first framed by SEELIGER. SEELIGER made use of the total number of stars from the brightest star to those of determined magnitude. SCHWARZSCHILD, however, uses the number of stars of each magnitude. This is already a great simplification. Besides his work is characterized by a severe mathematical treatment. His merit consists chiefly in giving an elegant general solution that is applicable to all fundamental problems of statistical astronomy [1]).

Let $N_h dh$ be the number of stars with an apparent brightness between h and $h + dh$ and π_h their mean parallax, then — if we indicate the density once more by $D(r)$ and the frequency curve of the absolute magnitudes by $\varphi(i)$ — the following relations are true:

$$N_h = 4\pi \int_0^\infty D(r)\, \varphi\,(hr^2)\, r^4\, dr \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{and } N_h\, \pi_h = 4\,\pi \int_0^\infty D(r)\, \varphi\,(hr^2)\, r^3\, dr \quad . \quad . \quad . \quad . \quad (2)$$

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[1]) His articles have appeared in *Astron. Nachr.* Nos. 4422, 4557 and 4740.

In *Astron. Nachr.* N°. 4422 the following problems were discussed:

a. Let N_h and $\varphi(i)$ be given. It is required to determine $D(r)$ by solving the integral equation (1).

b. Let N_h and π_h be given. It is required to determine both $D(r)$ and $\varphi(i)$ by solving simultaneously the integral equations (1) and (2).

The integral equations have been solved by SCHWARZSCHILD by means of the known properties of FOURIER coefficients [1].

It is clear that we can find the velocity law in an analogous way.

If it is required to determine simultaneously the density law, the luminosity law and the velocity law this can be done in the following ways:

$$
\begin{array}{llll}
1^{\text{st}} & \text{From } N'_m, & N_\mu \text{ and } & \tau_m, \\
2^{\text{nd}} & \text{,,} \quad N_m, & N_\mu \text{ ,,} & \pi_\mu, \\
3^{\text{rd}} & \text{,,} \quad N_m, & \pi_m \text{ ,,} & \pi_\mu, \\
4^{\text{th}} & \text{,,} \quad N'_\mu, & \pi_m \text{ ,,} & \pi_\mu.
\end{array}
$$

In case we suppose that there is no connection between luminosity and velocity, $N_{m,\mu}$ and $\mu_{m,\mu}$ would be sufficient data from which to determine the three functions we seek.

Practically we have to reckon with the accuracy with which the required data can be deduced from the observations. Theoretically we can find $D(r)$, $\varphi(i)$ and $\psi(V)$ in each of the cases mentioned by resolving the integral equations in accordance with SCHWARZSCHILD's method.

Serious objections, however, may be raised against the use of such integral formulae. If N_m, π_m, etc. were known to us as continuous analytical functions of the variables SCHWARZSCHILD's method would be very well adapted to the determining of the required functions from these data. As a rule, however, we only know the values of N_m and π_m for whole numbers of m. If now we represent these numbers by a formula, these relations, indeed, adapt themselves to interpolation. If, however, the relations have no theoretical foundations and the parameters no physical signification, we cannot attach any other value to them than that of interpolation formulae There is always the risk, then, that by using these relations, we keep properties of the original data hidden from view.

A second objection is that empirical relations are extrapolated out of the interval within which observations are available. If a function in a determined interval represents the observations with sufficient accuracy, it need not for that reason be of force outside the interval. And particularly with the integral method it can be determined

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[1] Vide also EDDINGTON, *Stellar Movements*, Chapter X.

only with great difficulty, how far the results are based on extra-
polation [1]).

Another drawback of the method is that we cannot inquire into
the dependence of $\varphi(i)$ or $\psi(V)$ on r. Moreover we are obliged
to assume that there is no such thing as absorption of the light
in space.

In SCHWARZSCHILD's application of his method it was not investi-
gated, how the density varies with the galactic latitude. This is,
however, possible, if we have sufficient data at our disposal.

Several objections that may be raised against SCHWARZSCHILD's
method do not exist with respect to KAPTEYN's method, with which
we dealt in a former communication.

Yet we have also derived from our data of observation the
frequency curve of absolute magnitudes in SCHWARZSCHILD's manner.
None of the methods proposed till now is entirely unassailable.
By applying methods based on different hypotheses we can judge
of the correctness of the suppositions that have been made and find
more reliable results.

A great advantage of SCHWARZSCHILD's method is that it distinctly
represents the connection of the different quantities and enables us
to judge, whether the values found for the unknown quantities
correspond to each other and form a consistent system.

In *Astron. Nachr.* N°. 4422 SCHWARZSCHILD has solved the two
problems above mentioned and has also given numerical results of
the unknown quantities. Use was made of the luminosity curve,
derived by KAPTEYN in *Astron. Journal* N°. 566 and of the numbers
N_m published by him in *Publ. Groningen* N°. 18. For $log. N_m$
SCHWARZSCHILD found:

$$log. N_m = 0.596 + 0.5612\, m - 0.0055\, m^2 \quad . \quad . \quad . \quad (3)$$

From these data the density was derived and the mean parallaxes π_m.

In his second article SCHWARZSCHILD investigated in which way
the chief stellar statistical quantities depend on the three principal
laws and gave formulae to calculate the different quantities. An
exact application of the method requires, when we use the general
form of the functions, a very comprehensive arithmetical labour.
This is only advisable if a very large amount of data of observation
are at our disposal. Therefore suppositions were made about the
form of the unknown functions.

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[1]) How one may obtain strange results by such unallowed extrapolation is seen,
for instance, when CHARLIER (*Meddelanden Observ. Lund,* Serie II, N⁰. 8, p. 21)
derives from the formula of KAPTEYN and SCHWARZSCHILD, which is cited in this
communication by (3), that the numbers N_m increase up to $m = 51$.

SCHWARZSCHILD supposes:

$$D(r) = 10^{a_0 - a_1 \rho - a_2 \rho^2} \qquad (\rho = -5.0 \; log. \; r)$$

$$\varphi(i) = 10^{b_0 - b_1 M - b_2 M^2} \qquad (M = -2.5 \; log. \; i)$$

$$\psi(V) = 10^{c_0 - c_1 G - c_2 G^2} \qquad (G = -5.0 \; log. \; V)$$

In contradistinction to the assumptions of SEELIGER about the form of the density law and the luminosity law these suppositions are not without any foundation. The form for $\varphi(i)$ has been found empirically by KAPTEYN and the form of the density function has been derived in *Astron. Nachr.* N°. 4422 by means of the numbers of stars of determined magnitude that have been counted. The form of the function $\psi(V)$ "ist zunächst rein formal der Bequemlichkeit der Rechnung wegen eingeführt". Besides the formula (3) mentioned above SCHWARZSCHILD deduced from the observations:

$$log. \; \pi_m = -1.108 - 0.125 \; m$$

$$log. \; \pi_{m, \mu} = -0.766 - R_1 \; m - 0.1243 \; g$$

in which g has been assumed to be $= -5.0 \; log. \; \mu$.

From these data the three principal laws and various other quantities, including the coefficient R_1, were derived.

According to SCHWARZSCHILD the distribution of luminosities found by him may also be formulated in this manner, that the absolute magnitudes are spread around the average value $11^m.5$ (in SCHWARZSCHILD's notation [1]) with a mean error of $3^m.8$ according to the law of errors. This is incorrect. From the data used by him it is easily found with the aid of the table of coefficients in *Astron. Nachr.* N°. 4557, that the mean M of his luminosity curve is $25^m.1$, therefore in KAPTEYN's notation $30^m.1$.

The frequency curve found by SCHWARZSCHILD differs considerably from the distribution of luminosities determined by KAPTEYN in *Publ. Groningen* N°. 11. This difference is puzzling as both investigators made use of the same data.

We have failed in finding a conclusive explanation for this bad agreement. One might think, that a correlation between the absolute magnitude and the velocity of the stars exerted its influence. Of late several investigators have indeed drawn the attention to some indications of a relation between luminosity and velocity. [2]). But yet one

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[1]) SCHWARZSCHILD makes use of the distance corresponding with $\pi = 1''$ as a unity of distance. Then $M = m + 5 \; log. \; \pi$, so that the relation $M_{KAPTEYN} = M_{SCHWARZSCHILD} + 5$ holds good.

[2]) Vide e.g. EDDINGTON, *Observatory* Vol. 38, p. 392, seq. Perhaps this question may also be solved by the investigation now in course of preparation at the Astronomical Laboratory at Groningen and on which we already drew the attention in our former communication.

may certainly not assume, that such a relation would be of so far-reaching importance and would have so great an influence on the result in applying SCHWARZSCHILD's method. Moreover, treating the data of observation available to us according to this method we found the same luminosity curve we had found according to KAPTEYN's method.

As there is no agreement, it seems to us, that KAPTEYN's result should be trusted most. His method is, indeed, to be preferred to SCHWARZSCHILD's and this chiefly for the following reasons:

1ˢᵗ. KAPTEYN does not suppose definite forms for the functions that are to be determined;

2ⁿᵈ. with KAPTEYN's method it is possible to examine, if the frequency function of absolute magnitudes is the same at all distances from the sun;

3ʳᵈ. if KAPTEYN's method is applied, it may be seen at once how far the results are based on observations and where extrapolation comes in;

4ᵗʰ. KAPTEYN's method need not be altered if it should appear that velocity is a function of luminosity, while SCHWARZSCHILD's formulae must undergo considerable modifications, and

5ᵗʰ. SCHWARZSCHILD's results depend to a high degree on the values of some quantities (e.g. the coefficient a_2) which can only with difficulty be derived with sufficient exactness from observations.

Yet SCHWARZSCHILD's method and KAPTEYN's if they are applied prudently to the same data, should give the same results. The difference found is probably to be attributed to the fifth objection that we raised against SCHWARZSCHILD's method.

The interpolation-formulae we deduced from our data for N_m and the formulae used by us for π_m and $\pi_{m,\mu}$ are to be trusted more than SCHWARZSCHILD's, because they are based on more complete and more minute data. Therefore less danger is to be apprehended from the objection mentioned for our determination. So it may perhaps be explained that SCHWARZSCHILD found a divergent result, as we attained the same results according to the different methods.

2. *The results of our investigation.*

We have applied SCHWARSCHILD's method to the same data of observation that we have also treated, as we have communicated in a former article, according to KAPTEYN's method.

The data we want are:

1. the numbers of stars of determined magnitude N_m,

2 the mean parallaxes of stars of determined magnitude π_m,

3. two coefficients of the formula for $\pi_{m,\mu}$.

We have established the mean luminosity law and also the mean density and velocity laws for the whole sky and moreover we have determined these principal laws for the 5 galactic zones separately.

The numbers N_m were derived from Table V of *Publ. Groningen* N°. 27. It was necessary to represent the numbers found by inter-polation-formulae. For these the following formulae were found:

Whole sky $\log. N_m = -4.2395 + 0.63812\,m - 0.011677\,m^2$
Zone   I $= -4.1848 + 0.65736 \quad\;\; - 0.011243$
     II $= -4.1841 + 0.63322 \quad\;\; - 0.011463$
     III $= -4.6159 + 0.71857 \quad\;\; - 0.017257$
     IV $= -4.4638 + 0.67891 \quad\;\; - 0.016289$
     V $= -4.5120 + 0.69565 \quad\;\; - 0.017976$

The mean parallaxes π_m, as we have already communicated, have been lent to us for our investigation with great kindness by Prof. KAPTEYN and Dr. VAN RHIJN. These may be represented as follows:

Whole sky $\log. \pi_m = 8.943 - 0.142\,m$
Zone   I $= 8.883 - 0.142\,m$
     II $= 8.904 - 0.142\,m$
     III $= 8.957 - 0.142\,m$
     IV $= 9.024 - 0.142\,m$
     V $= 9.066 - 0.142\,m$

We have deduced the mean parallaxes $\pi_{m,\mu}$ from those which KAPTEYN published in *Publ. Groningen* N°. 8, by making the constant a in the formula

$$\pi_{m,\mu} = a\mu^b \varepsilon^{m-5.0}$$

in agreement with the values of π_m just mentioned. Then we find the following formulae:

Whole sky $\log. \pi_{m,\mu} = -0.717 - 0.062\,m - 0.142\,g$
Zone   I $= -0.777 - 0.062\,m - 0.142\,g$
Zone   II $= -0.756 - 0.062\,m - 0.142\,g$
Zone   III $= -0.703 - 0.062\,m - 0.142\,g$
Zone   IV $= -0.636 - 0.062\,m - 0.142\,g$
Zone   V $= -0.594 - 0.062\,m - 0.142\,g$

We have derived the principal laws from these data according to the method that SCHWARZSCHILD has proposed in his article in *Astron. Nachr.* N°. 4557. There the relations, which exist between the coef-ficients of the different formulae, have been communicated *in extenso*. The whole computation has been made by means of the formulae

mentioned there. A possible relation between luminosity and velocity has been left out of consideration. Nor did we, imitating SCHWARZSCHILD make use of the coefficient of m in the formula for $\pi_{m,\mu}$. We mention here the results we found and also reprint for the sake of comparison the results that SCHWARZSCHILD found.

In all formulae we have used SCHWARZSCHILD's definition of absolute magnitude.

SCHWARZSCHILD's Results.

$$log.\, D(r) = + 0.488 - 0.097\, \varrho - 0.0088\, \varrho^2$$
$$log.\, \varphi(i) = - 2.879 + 0.737\, M - 0.0147\, M^2$$
$$log.\, \psi(V) = - 0.922 - 0.165\, G - 0.0581\, G^2$$
$$M_m = - 11.9 + 0.374\, m$$

Our Results for the whole sky.

$$log.\, D(r) = - 2.350 - 0.242\, \varrho - 0.0165\, \varrho^2$$
$$log.\, \varphi(i) = - 0.853 + 0.141\, M - 0.0403\, M^2$$
$$log.\, \psi(V) = - 1.331 - 0.611\, G - 0.1400\, G^2$$
$$M_m = - 7.9 + 0.290\, m$$

Zone I.

$$log.\, D(r) = - 3.113 - 0.263\, \varrho - 0.0158\, \varrho^2$$
$$log.\, \varphi(i) = - 0.902 + 0.154\, M - 0.0387\, M^2$$
$$log.\, \psi(V) = - 1.536 - 0.659\, G - 0.1344\, G^2$$
$$M_m = - 8.4 + 0.289\, m$$

Zone II.

$$log.\, D(r) = - 2.805 - 0.240\, \varrho - 0.0162\, \varrho^2$$
$$log.\, \varphi(i) = - 0.841 + 0.127\, M - 0.0397\, M^2$$
$$log.\, \psi(V) = - 1.603 - 0.727\, G - 0.1477\, G^2$$
$$M_m = - 8.2 + 0.289\, m$$

Zone III.

$$log.\, D(r) = - 4.103 - 0.402\, \varrho - 0.0244\, \varrho^2$$
$$log.\, \varphi(i) = - 0.646 + 0.025\, M - 0.0597\, M^2$$
$$log.\, \psi(V) = - 0.728 - 0.972\, G - 0.2074\, G^2$$
$$M_m = - 7.0 + 0.290\, m$$

Zone IV.

$$log.\, D(r) = - 3.690 - 0.332\, \varrho - 0.0230\, \varrho^2$$
$$log.\, \varphi(i) = - 0.671 + 0.057\, M - 0.0564\, M^2$$
$$log.\, \psi(V) = - 1.300 - 0.775\, G - 0.1958\, G^2$$
$$M_m = - 6.8 + 0.289\, m$$

Zone V.

$$log. D(r) = -4.207 - 0.362 \varrho - 0.0254 \varrho^2$$
$$log. \varphi(i) = -0.636 + 0.045 M - 0.0621 M^2$$
$$log. \psi(V) = -1.186 - 0.784 G - 0.2158 G^2$$
$$M_m = -6.4 + 0.290 m$$

The values we found for the various coefficients differ rather considerably from SCHWARZSCHILD's results. This is especially apparent in the formulae for $\varphi(i)$ and $\psi(V)$.

It is especially of importance to compare the luminosity curve with that of SCHWARZSCHILD and the frequency curves that were found for the various zones with each other. To facilitate this we have given another form to the formulae. In order to compare them we have also given KAPTEYN's results in the same form. Here too M has been expressed in the unit, used by SCHWARZSCHILD.

We represent the luminosity curve by the formula:

$$\varphi(M) = C e^{-h^2(M-k)^2}$$

A simple calculation shows us the relation between the new parameters and those used above.

The luminosity curves found above may be expressed now by formulae of the form we found, with the following values of the parameters:

	k	h
The whole sky . .	1.76	0.385
Zone I	2.00	0.378
Zone II	1.61	0.382
Zone III	0.21	0.469
Zone IV	0.51	0.456
Zone V	0.36	0.478
SCHWARZSCHILD . .	25.07	0.184
KAPTEYN [1] { type I	3.95	0.243
{ type II	5.30	0.247

The difference between the values found by us and those of SCHWARZSCHILD is very great, much greater than we had expected. There is more agreement with the results obtained by KAPTEYN, although here too at first sight the difference is pretty considerable. No great significance can be attributed, however, to the values found for k. These results are based on extrapolation as the parts of the frequency curves that are based on observations do not extend as far as the maximum. It appears from the figure that we added to this communication, that KAPTEYN's curve does not differ much from

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[1] *Astron. Journ.* N⁰. 566.

our determination as might perhaps be concluded from the values of k and h; but that the two curves agree very well.

No real significance can be ascribed to the maximum of the luminosity curves, determined by us, as the numbers for the magnitudes 5 and 6, etc. (notation of KAPTEYN) are based on the numbers which were found in the nearest vicinity of the sun. But our countings are not complete here, because we excluded stars with P.M. $> 50''$. To this may be ascribed the decrease in the numbers which we observed.

Very remarkable is the way in which the values for k agree that have been found for the different zones. It is true, there are indications of a systematic difference in the values of k for higher and less high galactic latitudes, but the differences between the values of the numbers are not so great, if we take into consideration the exactness of the data, that we can deduce from them with certainty, that the luminosity curves of the various galactic zones differ. How well the different curves agree, is most evident from the figure which we inserted in our first communication. The six lines in the upper part of the figure relate to the investigation now discussed.

We are of opinion that we may conclude with a tolerable degree of probability from these results that the frequency curve of absolute magnitudes does not vary with the galactic latitude. And if this should not be entirely correct, then the variation is certainly very small.

3. *Comparison with the results of other investigators.*

If we wish to compare the luminosity curves determined or assumed by different investigators in the course of time, then we can perform this best graphically. We have drawn the principal curves in the figure subjoined.

The curve with the indication "KAPTEYN" represents the luminosity law published in *Publ. Groningen* N°. 11. Our determination according to the same method, which we marked by the figure II, gave entirely the same result. They do not only agree in form, but the numbers of stars of every absolute magnitude which were found per unit of volume in the neighbourhood of the sun, are quite the same.

We added in order to make comparison possible a constant amount to each number $log. N_m$ for the other curves.

Then we have drawn the luminosity curve, that SCHWARZSCHILD deduced in *Astron. Nachr.* N°. 4557 and also the frequency function,
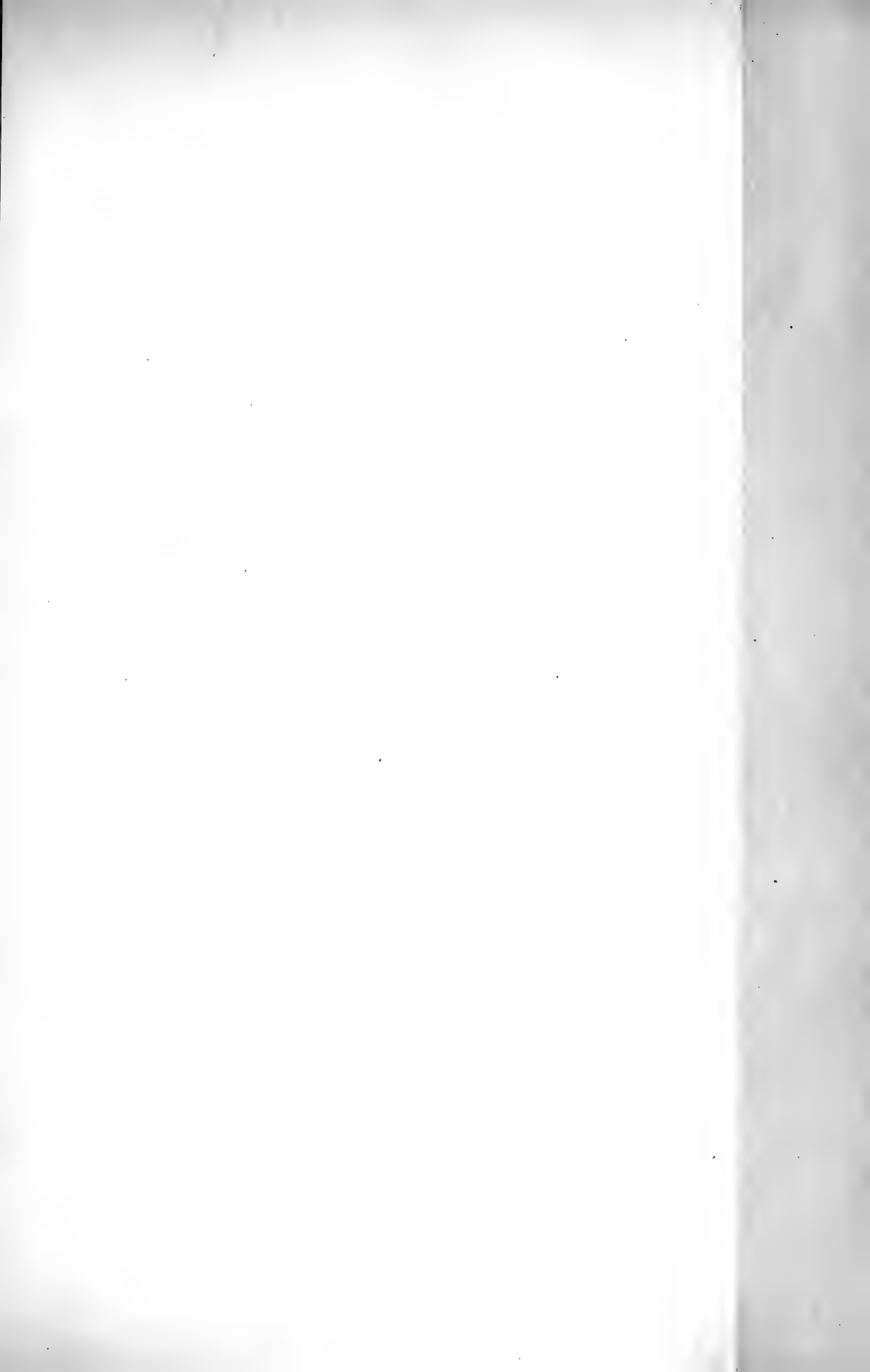
Log. Number.

+7.
+6.
+5.
+4
+3.
+2.
+1
0.
-1.
-2.
-3.
-4.
-5.
-6.
-7.
-8.

-8. -7. -6. -5. -4. -3. -2. -1. 0. +1. +2. +3. +4. +5. +6. +7. +8 Abs. Magn.

Walkey
Comstock
Dyson
Seeliger
Seeliger III
Seeliger IV
Seeliger II
Kapteyn
Schwartzschild
Schwarzschild
Schouten
Moll
Hertzsprung
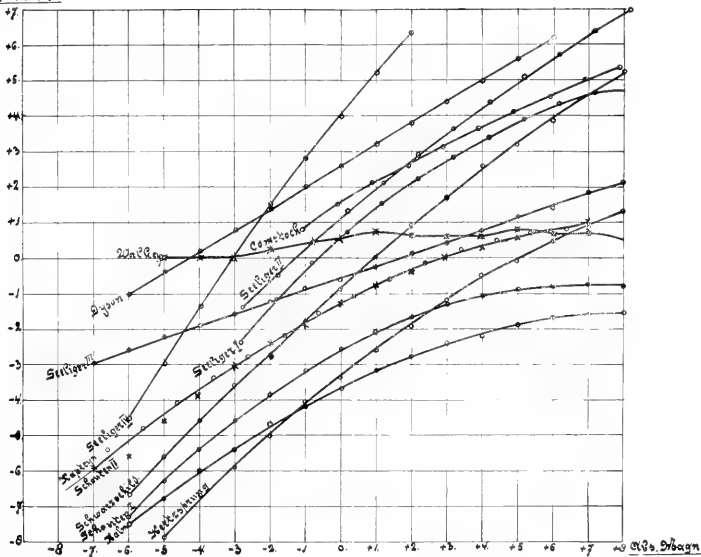
that we found according to the same method and marked by the figure I. Whereas the first is entirely different from KAPTEYN's luminosity law, the second agrees very well with it.

In *Astron. Nachr.* N°. 4422 HERTZSPRUNG assumed for the distribution function of absolute magnitudes a Gaussian curve with a mean value of $2^m.7$ and an average deviation of $\pm 3^m.0$.

HALM[1]) has assumed in his establishing of the luminosity law that the density is constant. He also supposes a perceptible extinction of the light in space. With the aid of these hypotheses the luminosity curve was deduced from the numbers of stars of determined magnitude found by CHAPMAN and MELOTTE and the mean parallaxes of KAPTEYN and COMSTOCK. It is remarkable that the curve found in this manner agrees pretty well with KAPTEYN's.

In *Monthly Notices* Vol. 72 DYSON has published an investigation founded on the cross components of the stars of CARRINGTON's Circumpolar Catalogue. Supposing that the density in the space taken up by these stars is everywhere the same, he determined the luminosity law. The curve found in this manner has been drawn by us.

COMSTOCK[2]) and WALKEY[3]) have derived the frequency function of absolute magnitudes from the luminosities of stars the parallax of which has been measured.

In his investigations on the structure of the universe SEELIGER has established the density law in the first place. This determination rests on the following theorem found by him[4]):

If, for $m < n$, $A_m \doteq Ch_m^{\frac{\lambda-3}{2}}$, the density D will be $= \gamma r^{-\lambda}$ whatever $\varphi(i)$ may be.

Here A_m means the number of stars from the brightest star to those of the magnitude m and h_m means the brightness of the stars of the apparent magnitude m, while r represents the distance from the sun.

We may formulate this theorem of SEELIGER also in this manner:

If the numbers of stars of determined magnitude form a geometrical progression, the density is proportional to a negative power of r.

We have proved in our thesis for the doctorate[5]), that several

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[1]) *Monthly Notices*, Vol. 77.

[2]) *Astron. Journ.* N°. 569.

[3]) *Astron. Nachr.* N°. 4754.

[4]) The demonstration given by SEELIGER is very intricate. We have published, however, in our doctoral dissertation a very simple proof, which we owe to Prof KAPTEYN.

[5]) On the Determination of the Principal Laws of Statistical Astronomy. Amsterdam, KIRCHNER. 1918.

objections may be raised against the general validity of this theorem. SEELIGER thought the premise of his theorem was affirmed by observations. This conclusion was premature and appears to be incorrect by comparison with more exact data. Therefore the density law derived by SEELIGER cannot be accepted. And also his considerations on a limit of the sidereal system found by him fail in sufficient foundation.

SEELIGER determined the luminosity law by solving an integral equation well-known in stellar astronomy by means of the density found. No great significance can be attributed to the result derived in this way.

For the luminosity law, we indicated by "SEELIGER I", use was made of the density law $D(r) = \gamma \, r^{-\lambda}$, while in establishing the curve "SEELIGER II" he represented the density by $D(r) = \gamma^{-\lambda} - \alpha \, r^{-\lambda_1}$. No sufficient motives have been stated for this last form. Moreover n both determinations a definite form of the function $\varphi(i)$ was presupposed, which is undesirable and unnecessary.

The curve in our figure with the indication "SEELIGER III" has not been deduced by SEELIGER; but it is a consistency of his theory. If we extend namely — as Prof. KAPTEYN observed — SEELIGER's theorem to stars fainter than the limiting magnitude [1]), then we find:

If, for $m > n$, $A_m = C h_m^{\frac{\lambda-3}{2}}$, then $\varphi(i) = A i^{\frac{3-\lambda}{2}}$ independent of $D(r)$.

We now find according to *Publ. Groningen* N°. 27 for $12.0 < m < 16.0$ with some approximation:

$$log. \; A_m = 1.797 + 0.340 \, (m-12).$$

This gives the luminosity curve $\varphi(i) = A i^{0.85}$, which we indicated in the figure by "SEELIGER III".

The graphical representation indicates how much the frequency curves found by different investigators differ mutually. All the more it is of importance to observe that our independent investigation furnished a perfect affirmation of the luminosity law deduced by Prof. KAPTEYN in 1901 from the data still so scanty at that time.

Kampen, September 1918.

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[1]) The value of n is according SEELIGER about 11.5.

Astronomy. — *"The longitude of Hyperion's pericentre and the mass of Titan"*. By Dr. J. WOLTJER JR. (Communicated by Prof. **W.** DE SITTER).

(Communicated in the meeting of December 28, 1918).

1. In my dissertation [1]), published in the course of this year, I commenced the determination of the action of Titan on the motion of Hyperion. The developments include the libration in the critical argument, in the semi-axis major and in the eccentricity, together with a determination of the mean motion of the argument of the libration; further the large inequality of the critical argument, proportional to the first power of Titan's eccentricity. As I intend to carry on these computations, the first thing to be done is to determine the libration in the longitude of pericentre and the mean motion of this element. The results are contained in this paper, which forms a continuation of the memoir already cited.

To this end the development of the perturbative function ("Investigations" Chapter I) has to be continued by the computation of the derivative with respect to e, the eccentricity of Hyperion. The determination of the derivative with respect to a, the semi-axis major, being closely related to this computation, we also shall derive this function, though not required for the purpose of this paper.

To check the special values of the perturbative function used for these developments, an independent computation of the same values has been carried out, starting from the goniometric development of the square of the mutual distance of the two satellites. The greater part of the numerical computations involved has been performed by Mr. D. GAIJKEMA, computer at the Leiden Observatory.

2. The determination of the derivative of the perturbative function with respect to e consists of the computation of the function

$$\frac{\partial f([1])}{\partial e},$$

_____

[1]) "Investigations in the theory of Hyperion"; hereafter to be cited as "Investigations".

$f([1])$ being the function defined in the first chapter of the "Investigations". From this definition results (with the notation of this chapter):

$$\frac{\partial f([1])}{\partial e} = \frac{1}{2\pi}\int_0^{2\pi} \frac{\partial}{\partial e}\frac{a'}{\Delta}\, d[3]. \tag{1}$$

For a given value of $[1]$ the quantity $\dfrac{\partial}{\partial e}\dfrac{a'}{\Delta}$ (which is a function of $[1]$ and $[3]$ only, as regards the angular variables) can be developed thus:

$$\left.\begin{aligned}\frac{\partial}{\partial e}\frac{a'}{\Delta} &= p_o + p_1\cos[3] + p_2\cos 2[3] + \ldots + p_n\cos n[3] + \ldots\\ &\quad + q_1\sin[3] + q_2\sin 2[3] + \ldots + q_n\sin n[3] + \ldots\end{aligned}\right\} \tag{2}$$

Then we have:

$$\frac{\partial f([1])}{\partial e} = p_o, \tag{3}$$

and:

$$\frac{1}{n}\sum_{s=0}^{n-1}\left(\frac{\partial}{\partial e}\frac{a'}{\Delta}\right)_s = p_o + p_n + p_{2n} + p_{3n} + \ldots, \tag{4}$$

$\left(\dfrac{\partial}{\partial e}\dfrac{a'}{\Delta}\right)_s$ being the value of $\dfrac{\partial}{\partial e}\dfrac{a'}{\Delta}$ for $[3] = \dfrac{2\pi}{n}s$.

Thus:

$$\frac{\partial f([1])}{\partial e} = \frac{1}{n}\sum_{s=0}^{n-1}\left(\frac{\partial}{\partial e}\frac{a'}{\Delta}\right)_s - p_n - p_{2n} - p_{3n} - \ldots \tag{5}$$

We are able to judge of the magnitude of the coefficients p_n for large values of n by considering the mean values

$$\frac{1}{n}\sum_{s=0}^{n-1}\left(\frac{\partial}{\partial e}\frac{a'}{\Delta}\right)_s,$$

for different values of n. Choosing $n = 270,\ 135,\ 90,\ 54$ and $[1] = 0°$ and taking for the constants e and $\dfrac{a'}{a}$ the values of the table on page 3 of the "Investigations", I get:

$$n = 270 \qquad \frac{1}{n}\sum_{s=0}^{n-1}\left(\frac{\partial}{\partial e}\frac{a'}{\Delta}\right)_s .\, 10^4 = -\,108614$$

$$135 \qquad\qquad\qquad -\,108614$$

$$90 \qquad\qquad\qquad -\,108614$$

$$54 \qquad\qquad\qquad -\,108616.$$

From these values results:

$$p_0 + p_{270} + \ldots = p_0 + p_{135} + p_{270} + \ldots = p_0 + p_{90} + p_{180} + \ldots; \quad (6)$$

and thus:

$$p_{135} = 0, \qquad\qquad p_{90} = 0, \qquad\qquad p_{54} = -2.10^{-5}. \quad (7)$$

Supposing the coefficients p_n for large values of n to be of this order of magnitude also if $[1] \neq 0°$, we see that we are allowed to use the formula

$$\frac{\partial f([1])}{\partial e} = \frac{1}{n} \sum_{s=0}^{n-1} \left(\frac{\partial}{\partial e} \frac{a'}{\Delta} \right)_s, \quad (8)$$

without, on this account, having to fear an error in the resulting value of $\dfrac{\partial f([1])}{\partial e}$ larger than half a unit of the fifth decimal, if $n \geq 90$.

In the next table I have collected the values of $\dfrac{\partial f([1])}{\partial e}$, computed according to this formula; for $[1] = 0°$ I took $n = 270$, for the other values of $[1]$ $n = 135$; the values of the constants e and $\dfrac{a'}{a}$ are those of the table on page 3 of the "Investigations".

$[1]$	$\dfrac{\partial f([1])}{\partial e} \cdot 10^5$
0°	-108614
$+8°$	-108574
$+16°$	-108450
$+24°$	-108226
$+32°$	-107877
$+36°$	-107647

The function $\dfrac{\partial f([1])}{\partial e}$ is an even function of $[1]$; putting $[1] = q \sin w$, q being a constant, the development becomes:

$$\frac{\partial f([1])}{\partial e} = \psi(w) = \sum_{n=0}^{\infty} k_{2n} \cos 2\, nw. \quad (9)$$

I take $q = +36°$, thus putting $[1] = +36° \sin w$; if from this last equation we compute a value of w in the first quadrant for each value of $[1]$ from the preceding table, we have the value of $\psi(w)$ for six values of w and thus six linear equations, from which,

putting k_{1_2}, k_{1_4}, ..., etc. zero, $k_{0}, k_2, ..., k_{1_6}$ can be solved. The coefficients k_8 and k_{1_6} appear to be zero and the following development of $\psi (w)$ results:

$$10^5 \cdot \frac{\partial f ([1])}{\partial e} = 10^5 \cdot \psi (w) = - 108151$$

$$- 484 \quad \cos 2\, w$$
$$+ 21 \quad \cos 4\, w \quad (10)$$
$$+ 1 \quad \cos 6\, w\, .$$

3. The derivative of the function $f([1])$ with respect to a is determined by the formula

$$a \frac{\partial f ([1])}{\partial a} = \frac{1}{2\pi} \int_0^{2\pi} a \frac{\partial}{\partial a} \frac{a'}{\Delta} d [3]\, . \qquad (11)$$

For a given value of $[1]$ the quantity $a \dfrac{\partial}{\partial a} \dfrac{a'}{\Delta}$ can be developed thus:

$$a \frac{\partial}{\partial a} \frac{a'}{\Delta} = p_0 + p_1 \cos [3] + p_2 \cos 2 [3] + \ldots + p_n \cos n [3] + \ldots$$
$$+ q_1 \sin [3] + q_2 \sin 2 [3] + \ldots + q_n \sin n [3] + \ldots \qquad (12)$$

Thus:

$$a \frac{\partial f ([1])}{\partial a} = \frac{1}{n} \sum_{s=0}^{n-1} \left(a \frac{\partial}{\partial a} \frac{a'}{\Delta} \right)_s - p_n - p_{2n} - p_{3n} - \ldots \qquad (13)$$

Again we derive the mean values $\dfrac{1}{n} \sum\limits_{s=0}^{n-1} \left(a \dfrac{\partial}{\partial a} \dfrac{a'}{\Delta} \right)_s$ for the values $n = 270, 135, 90, 54$ and the value $[1] = 0°$. The values of the constants e and $\dfrac{a'}{a}$ are those of the table on page 3 of the "Investigations". We get:

$$n = 270 \qquad \frac{1}{n} \sum_{s=0}^{n-1} \left(a \frac{\partial}{\partial a} \frac{a'}{\Delta} \right)_s \cdot 10^5 = - 110691$$
$$135 \qquad\qquad\qquad\qquad\qquad\qquad - 110691$$
$$90 \qquad\qquad\qquad\qquad\qquad\qquad - 110691$$
$$54 \qquad\qquad\qquad\qquad\qquad\qquad - 110706\, .$$

Thus:

$$p_o + p_{270} + \ldots = p_o + p_{135} + p_{270} + \ldots = p_o + p_{90} + p_{180} + \ldots;\qquad (14)$$

and:

$$p_{270} = 0, \qquad p_{135} = 0, \qquad p_{90} = 0;\qquad (15)$$

further:

$$p_{54} = -15 . 10^{-5} . \tag{16}$$

Supposing the coefficients p_n for large values of n to be of this order of magnitude also if $[1] \neq 0°$, we see that we are allowed to use the formula

$$a \frac{\partial f([1])}{\partial a} = \frac{1}{n} \sum_{s=0}^{n-1} \left(a \frac{\partial}{\partial a} \frac{a'}{\Delta} \right)_s , \tag{17}$$

without, on this account, having to fear an error in the resulting values of $a \dfrac{\partial f([1])}{\partial a}$ larger than half a unit of the fifth decimal, if $n \geqq 90$.

In the next table I have collected the values of $a \dfrac{\partial f([1])}{\partial a}$, computed according to this formula; for $[1] = 0°$ I took $n = 270$, for the remaining values of $[1]$ $n = 135$; the values of the constants e and $\dfrac{a'}{a}$ are those of the table on page 3 of the "Investigations".

$[1]$	$a \dfrac{\partial f([1])}{\partial a} . 10^5$
$0°$	$- 110691$
$+ 8°$	$- 110887$
$+ 16°$	$- 111477$
$+ 24°$	$- 112480$
$+ 32°$	$- 113921$
$+ 36°$	$- 114820$

The function $a \dfrac{\partial f([1])}{\partial a}$ is an even function of $[1]$; putting $[1] = = q \sin w$, q being a constant, the development becomes:

$$a \frac{\partial f([1])}{\partial a} = \lambda (w) = \sum_{n=0}^{\infty} l_{2n} \cos 2n \, w . \tag{18}$$

I take $q = + 36°$, thus putting $[1] = + 36° \sin w$; if from this last equation we compute a value of w in the first quadrant for each value of $[1]$ from the preceding table, we have the value of $\lambda(w)$ for six values of w and thus six linear equations, from which, putting $l_{12}, l_{14}, \ldots$, etc. zero, $l_0, l_2, \ldots, l_{10}$ can be solved. The coefficients l_6, l_8 and l_{10} appear to be zero and the following development of $\lambda(w)$ results:

$$a \frac{\partial f\,([1])}{\partial a} \cdot 10^\mathsf{s} = \lambda\,(w) \cdot 10^\mathsf{s} = \left. \begin{array}{l} -112732 \\ + 2064 \quad cos\,2\,w \\ -\ 23 \quad cos\,4\,w. \end{array} \right\} \qquad (19)$$

4. The first system of differential equations of Chapter II § 3 of the "Investigations" contains the equations for the determination of the four variables ϱ, σ, θ, Ω, supposing TITAN's eccentricity to be zero. The remaining part of Chapter II contains the determination of those terms of the variables ϱ, σ, θ, which are of order zero and one with respect to $\sqrt{\dfrac{m'}{M}}$. To complete the computations we shall examine the last equation of the system mentioned, viz. the equation for Ω. This equation:

$$\frac{d\Omega}{dt} = -\frac{\partial R_1}{\partial \sigma}, \qquad (20)$$

can be written thus:

$$\frac{d\Omega}{dt} = -\frac{m'}{a'}\frac{\partial f}{\partial \sigma}. \qquad (21)$$

As ϱ, σ and θ are known functions of t, the solution of this equation is reduced to a quadrature.

The right member of the equation is an even function of θ; substituting the series from Chapter II § 3 of the "Investigations" for ϱ, σ, θ, this right member gets the form:

$$\mu^\mathsf{s} \overset{p=\infty}{\underset{p=0}{\Sigma}} \Phi_p\,\mu^p; \qquad (22)$$

here $\mu = \sqrt{\dfrac{m'}{M}}$ and Φ_p is an even periodic function of τ.

Denoting the constant term of the goniometric development of Φ_p with respect to τ by $\overline{\Phi}_p$, we have:

$$\frac{d\Omega}{dt} = \mu^\mathsf{s} \overset{p=\infty}{\underset{p=0}{\Sigma}} \overline{\Phi}_p\,\mu^p + \mu^\mathsf{s} \overset{p=\infty}{\underset{p=0}{\Sigma}} (\Phi_p - \overline{\Phi}_p)\,\mu^p, \qquad (23)$$

and thus:

$$\Omega = \text{constant} + \mu^\mathsf{s}\,t \overset{p=\infty}{\underset{p=0}{\Sigma}} \overline{\Phi}_p\,\mu^p + \frac{\mu^\mathsf{s}}{v} \overset{p=\infty}{\underset{p=o}{\Sigma}} \mu^p \int\limits_0^\tau (\Phi_p - \overline{\Phi}_p)d\tau. \qquad (24)$$

Developing the divisor v according to the series (Chapter II § 3)

$$v = \overset{p=\infty}{\underset{p=1}{\Sigma}} v_p\,\mu^p,$$

Ω gets equal to the expression:

$$\Omega = \varpi + \sum_{p=0}^{p=\infty} \Omega_p \left(\sqrt{\frac{m'}{M}} \right)^p,$$

$$\Omega_p = \sum_{s=1}^{s=\infty} \Omega^{(p,s)} \sin s\tau, \qquad p = 0,1,\ldots,$$

$$\varpi = \text{constant} + \chi\,t,$$

$$\chi = \frac{m'}{M} \sum_{p=0}^{p=\infty} \chi_{p+2} \left(\sqrt{\frac{m'}{M}} \right)^p.$$

(25)

Deviating from the notation of the "Investigations" I have denoted the coefficient of t in ϖ by the letter χ, to prevent confusion with the known number π.

We get:

$$\Omega_{\scriptscriptstyle 0} = 0,$$

$$\Omega_1 = -\frac{1}{v_1}\frac{M}{a'} \int_0^\tau \left(\left[\frac{\partial f}{\partial \sigma}\right]_{\rho_0 \sigma_0 \theta_0} - \overline{\left[\frac{\partial f}{\partial \sigma}\right]_{\rho_0 \sigma_0 \theta_0}} \right) d\tau,$$

(26)

$$\chi_{\scriptscriptstyle 2} = -\frac{M}{a'} \overline{\left[\frac{\partial f}{\partial \sigma}\right]_{\rho_0 \sigma_0 \theta_0}},$$

denoting the constant term of the periodic development of $\left[\dfrac{\partial f}{\partial \sigma}\right]_{\rho_0 \sigma_0 \theta_0}$ with respect to τ by a stroke above the functional sign.

As

$$\frac{\partial a}{\partial \sigma} = 0, \qquad \frac{\partial e}{\partial \sigma} = -\frac{\sqrt{1-e^2}}{e}\frac{1}{\sqrt{aM}},$$

(27)

we get:

$$\frac{\partial f}{\partial \sigma} = -\frac{\partial f}{\partial e}\frac{\sqrt{1-e^2}}{e}\frac{1}{\sqrt{aM}};$$

(28)

hence:

$$\chi_{\scriptscriptstyle 2} = \frac{\sqrt{1-e_0^2}}{e_0}\sqrt{\frac{a'}{a_0}}\,n'_{\scriptscriptstyle 0} \overline{\left[\frac{\partial f}{\partial e}\right]_{\rho_0 \sigma_0 \theta_0}},$$

$$\Omega_1 = \frac{\sqrt{1-e_0^2}}{e_0}\sqrt{\frac{a'}{a_0}}\frac{n'_{\scriptscriptstyle 0}}{v_1} \int_0^\tau \left(\left[\frac{\partial f}{\partial e}\right]_{\rho_0 \sigma_0 \theta_0} - \overline{\left[\frac{\partial f}{\partial e}\right]_{\rho_0 \sigma_0 \theta_0}} \right) d\tau.$$

(29)

For the coefficients substituting their numerical values, we get:

$$\chi_{\scriptscriptstyle 2} = + [0.937584]\,n'_{\scriptscriptstyle 0} \overline{\left[\frac{\partial f}{\partial e}\right]_{\rho_0 \sigma_0 \theta_0}},$$

$$\Omega_1 = + [2.499354]^{(0)} \int_0^\tau \left(\left[\frac{\partial f}{\partial e}\right]_{\rho_0 \sigma_0 \theta_0} - \overline{\left[\frac{\partial f}{\partial e}\right]_{\rho_0 \sigma_0 \theta_0}} \right) d\tau;$$

(30)

the numbers in brackets are logarithms; Ω_1 has been expressed in degrees, which fact has been denoted by the symbol (0).

The quantity χ_3 can be determined by the equation:

$$\chi_3 = -\frac{M}{a'}\left\{\left[\overline{\frac{\partial^2 f}{\partial\sigma\partial\varrho}}\right]_0 \varrho_1 + \left[\overline{\frac{\partial^2 f}{\partial\sigma^2}}\right]_0 \sigma_1 + \left[\overline{\frac{\partial^2 f}{\partial\sigma\partial\theta}}\right]_0 \theta_1\right\}, \qquad (31)$$

the symbol $[\ ]_0$ being an abbreviation for $[\ ]_{\varrho=\varrho_0,\ \sigma=\sigma_0,\ \theta=\theta_0}$.

The right member is the constant term of an even periodic function of τ, which changes its sign if τ is replaced by $\pi-\tau$. Thus:

$$\chi_3 = 0. \qquad (32)$$

5. The development of the function $\dfrac{\partial f([1])}{\partial e}$ from § 2 of this paper enables us to compute the numerical value of Ω_1 and χ_2. To derive the function $\left[\dfrac{\partial f}{\partial e}\right]_{\varrho_0\sigma_0\theta_0}$, the variable w is to be expressed as function of τ in the development of $\dfrac{\partial f([1])}{\partial e}$ as function of w according to formula (10).

From the relation (Investigations p. 26)

$$w + x \sin 2w = \tau, \qquad x = +0.00318,$$

results:

$$\cos p\,w = \cos p\,\tau - \frac{p}{2}\,x\,\{\cos(p+2)\,\tau - \cos(p-2)\,\tau\} + \{..\}\,x^2 + ..; \qquad (33$$

and thus:

$$\left.\begin{array}{l}\cos 2w - \cos 2\tau = +0.0032 - 0.0032\cos 4\tau,\\[4pt]\cos 4w - \cos 4\tau = +0.01\cos 2\tau - 0.01\cos 6\tau.\end{array}\right\} \qquad (34)$$

With aid of these formulas the following value for the development of $\left[\dfrac{\partial f}{\partial e}\right]_{\varrho_0\sigma_0\theta_0}$, as function of τ, can be deduced:

$$\left.\begin{array}{l}\left[\dfrac{\partial f}{\partial e}\right]_{\varrho_0\sigma_0\theta_0} . 10^5 = -108153\\[8pt]\qquad\qquad -484 \quad \cos 2\,\tau\\[6pt]\qquad\qquad +23 \quad \cos 4\,\tau\\[6pt]\qquad\qquad +1 \quad \cos 6\,\tau.\end{array}\right\} \qquad (35)$$

Thus:

$$\left.\begin{array}{l}\left[\overline{\dfrac{\partial f}{\partial e}}\right]_{\varrho_0\sigma_0\theta_0} . 10^5 = -108153\,;\\[14pt]10^5 . \displaystyle\int_0^\tau\left\{\left[\dfrac{\partial f}{\partial e}\right]_{\varrho_0\sigma_0\theta_0} - \left[\overline{\dfrac{\partial f}{\partial e}}\right]_{\varrho_0\sigma_0\theta_0}\right\}\,d\tau = -242\sin 2\tau + 6\sin 4\tau.\end{array}\right\} \qquad (36)$$

Substituting these expressions in the formula (30), we get the results collected in the next table.

$$\Omega_1 = \sum_{s=1}^{\infty} \Omega^{(1,s)} \sin s\tau$$

$$\Omega_1 = -0°.765 \sin 2\tau + 0°.019 \sin 4\tau$$

$$\Omega^{(1,2s-1)} = 0 \quad s = 1,2,\ldots$$

$$\chi_2 = -9.3675 \, n'_0$$

6. With regard to future developments we shall determine the derivatives of the functions Ω_1 and χ_2 (considered as functions of ϱ_0, σ_0, q and τ) with respect to q; to this purpose we need the value of the function

$$\frac{\partial}{\partial q}\left[\frac{\partial f}{\partial e}\right]_{\rho_0\sigma_0\theta_0},$$

which value is given by the equation

$$\frac{\partial}{\partial q}\left[\frac{\partial f}{\partial e}\right]_{\rho_0\sigma_0\theta_0} = \left[\frac{\partial^2 f}{\partial e\partial\theta}\right]_{\rho_0\sigma_0\theta_0}\frac{\partial\theta_0}{\partial q}. \tag{37}$$

For the determination of the function $\dfrac{\partial^2 f}{\partial e\partial\theta}$ we have the formulas:

$$q\frac{\partial \cos 2w}{\partial\theta} = -4\sin w,$$

$$q\frac{\partial \cos 4w}{\partial\theta} = +8\sin w - 8\sin 3w, \tag{38}$$

$$q\frac{\partial \cos 6w}{\partial\theta} = -12\sin w + 12\sin 3w - 12\sin 5w.$$

Hence:

$$10^5 \cdot q\frac{\partial^2 f}{\partial e\partial\theta} = +2092\ \sin w - 156\ \sin 3w - 12\ \sin 5w. \tag{39}$$

For the development of the goniometric functions of the different multiples of w as functions of τ, in the first place we have the formula (Investigations p. 27):

$$\sin w = +0.99841 \sin\tau - 0.00159 \sin 3\tau.$$

Further from the relation (see section N°. 5)
$$w + x \sin 2 w = \tau, \qquad x = + 0.00318,$$
we deduce:
$$\sin p \, w = \sin p\tau - \frac{p}{2} x \{ \sin (p+2)\tau - \sin (p-2)\tau \} + \{ .. \} x^2 + \dots \quad (40)$$
and thus:
$$\sin 3 w - \sin 3 \tau = + 0.005 \sin \tau - 0.005 \sin 5 \tau . \quad (41)$$
With aid of these formulas we deduce:
$$10^6 \cdot q \left[\frac{\partial^2 f}{\partial e \partial \theta} \right]_{\rho_0 \tau_0 \theta_0} = \left. \begin{array}{l} + 2088 \quad \sin \tau \\[4pt] - 159 \quad \sin 3 \tau \\[4pt] - 11 \quad \sin 5 \tau. \end{array} \right\} \quad (42)$$

In connection with this formula, from the table for $\dfrac{\partial \theta_\bullet}{\partial q}$ on page 33 of the "Investigations", the relation results:
$$10^5 \cdot q^2 \left[\frac{\partial^2 f}{\partial e \partial \theta} \right]_{\rho_0 \tau_0 \theta_0} \frac{\partial \theta_\bullet}{\partial q} = \left. \begin{array}{l} + 653 \\[4pt] - 706 \quad \cos 2\tau \\[4pt] + 49 \quad \cos 4 \tau \\[4pt] + 3 \quad \cos 6 \tau . \end{array} \right| \quad (43)$$

Hence:
$$\left. \begin{array}{l} 10^6 \cdot q^2 \dfrac{\partial}{\partial q} \left[\overline{\dfrac{\partial f}{\partial e}} \right]_{\rho_0 \tau_0 \theta_0} = + 653 , \\[14pt] 10^6 \cdot q^2 \dfrac{\partial}{\partial q} \displaystyle\int_0^\tau \left\{ \left[\dfrac{\partial f}{\partial e} \right]_{\rho_0 \tau_0 \theta_0} - \left[\overline{\dfrac{\partial f}{\partial e}} \right]_{\rho_0 \tau_0 \theta_0} \right\} d\tau = - 353 \sin 2\tau + 12 \sin 4\tau. \end{array} \right\} \quad (44)$$

The values of $\dfrac{q}{\chi_2} \dfrac{\partial \chi_2}{\partial q}$ and $q \dfrac{\partial \Omega_1}{\partial q}$ result from formula (30). I collect these values in the next table. Deriving these values, we ought to

$\dfrac{\partial \Omega_1}{\partial q} = \displaystyle\sum_{s=1}^{\infty} \dfrac{\partial \Omega^{(1,s)}}{\partial q} \sin s\tau$
$q \dfrac{\partial \Omega_1}{\partial q} = - 0.0305 \sin 2\tau + 0.0010 \sin 4\tau$
$\dfrac{q}{\chi_2} \dfrac{\partial \chi_2}{\partial q} = - 0.00961$

remember that the numerical coefficient of the integral in the formula for Ω_1 also depends on q.

7. From the value of χ_2 of section N° 5 we shall derive a value of the mass of Titan. Taking account of the equation $\chi_3 = 0$, for the motion of Hyperion's pericentre, neglecting terms of the order $\left(\dfrac{m'}{M}\right)^2$, we get:

$$- 9.3675\, n'_{\bullet}\, \frac{m'}{M}\,. \tag{45}$$

From observation H. Struve [1]) for the mean motion of Hyperion's pericentre gets the value:

$$- 18.°663\,;$$

correcting for precession, we get:

$$- 18.°677\,;$$

here the Julian year is the unit of time.

Before comparing the theoretical value according to formula (45) with the observed motion, we ought to correct the latter on account of the secular variations caused by the sun, Saturn's ellipticity and the other satellites. According to H. Samter [1]) the values of these variations are respectively $+ 0.°011$, $+ 0.°234$ and $+ 0.°009$ a year. Subtracting the sum of these numbers from the observed motion, the equation for the determination of Titan's mass becomes:

$$- 9.3675\, n'_{\bullet}\, \frac{m'}{M} = - 18.°931\,. \tag{46}$$

As n'_0 differs from n' only in the terms of order $\dfrac{m'}{M}$ and higher, I put $n'_0 = n'$ and thus:

$$n'_0 = 365.25 \times 22.°5770\,.$$

Then from (46) we get:

$$\frac{M}{m'} = 4080\,.$$

This value agrees quite well with the value from the mean motion

[1]) Beobachtungen der Saturnstrabanten. Publications de l'Observatoire Central Nicolas. Série II. Vol. XI. 1898. p. 290.

[1]) Die Masse des Saturnstrabanten Titan. Sitz. Ber. der Kön. Pr. Akad. der Wissenschaften. 1912.

of the argument of the libration (Investigations p. 70) (which value also has been derived on simplifying suppositions), viz.:

$$\frac{M}{m'} = 3986 .$$

The values of $\frac{M}{m'}$ computed by EICHELBERGER and SAMTER from the perturbations of Hyperion are:

W. S. EICHELBERGER: 4172 ± 58,

H. SAMTER: 4125 .

Thus the agreement of the different values is satisfactory.

Chemistry. — *"On the influence of some salts on the dyeing of cellulose with Benzopurpurin 4B"*. By Prof. J. Böeseken, Miss G. W. Tergau and A. C. Binnendijk.

(Communicated in the meeting of Nov. 30, 1918).

I.

The object of this investigation was originally to examine whether the function of the salts in dyeing cellulose with benzidin dyestuffs was of a catalytic or of another nature.

I had found with v. d. Berg and Kerstjens [1]) that in acetylating cellulose with acetic acid anhydride, the action of H_2SO_4 and iodine was purely catalytic, as small quantities of these substances were sufficient to induce the attack of the very complicated cellulose molecule. As cellulose is entirely insoluble in acetic acid anhydride, the substances mentioned above formed the bridge on which the cellulose and the anhydride could meet and react on each other. It was not out of the question that the anorganic salts acted the same part between dyestuff and fibre material as sulphuric acid between anhydride and cellulose, as far as they enabled the dyestuff to enter the fibre substance.

However it was already evident from the literature on this subject that one must not speak of a catalytic action, because the metal-atoms of the salts added were taken up by the fibre material, in quantities which are almost equivalent to the dyestuff (as a bisulphonic acid).

. It was also known that if one wants the benzopurpurin to be taken up properly by cotton wool, then there must be present in the dye-bath a quantity of salt greater than an equimolecular one in regard to purpurin ; this does not strike one at once because the molecular weight of the purpurin is great (680) and the dyestuff solutions are frequently very diluted. In fact the phenomenon may better be compared with the salting out of soaps and is considered to be a shaking out by the fibre substance of the dyestuff salt soluble in it, of which salt the concentration in the bath is considerably increased by the addition of alcali-salt.

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[1]) Recueil **35**, 320 (1916).

Some preliminary experiments showed that the quantities of salt necessary for the exhaustion of the dye-bath were indeed *much* greater than equimolecular; thus a solution of 1 mg. of benzopurpurin in 100 ccm. H_2O or of $^1/_{68}$ millimol. needed 500 mgr. Na_2SO_4, *viz.* nearly 40 millimol. in order to be exhausted by 1 gram of cotton-wool.

This was affirmed with a whole series of other salts; in every case the quantity of salt necessary to bring about an almost entire decoloration of the bath was many times greater than the quantity of benzopurpurin.

As at the same time observations were made which might throw a light on the dyeing process, the investigation was continued in a quantitative way with a number of metal salts.

The preliminary experiments were executed with solutions of 1 milligram of pure (salt free) benzopurpurin 4B and, in relation to each other, equimolecular quantities of a number of salts, in 100 ccm. H_2O. Every time 1 gram of purified cotton-wool, which had been freed from fat, was exposed in porcelain cups during 10 minutes to the action of these solutions at 65°. It appeared that the intensity of colour of the bath, while using sulphates of sodium, potassium and ammonium was almost identical, but still not *completely* so.

Salt.	Quantity.	Effect.
$(NH_4)_2 SO_4$	0.0661 gr.	Little difference; decreasing as indicated by the arrow
$Na_2 SO_4$ 10 aq.	0.1612 „	
$K_2 SO_4$	0.0872 „	↓
$Mg SO_4$	0.0602 „	markedly lighter
$Al_2 (SO_4)_3$	0.1111 „	precipitated in the bath

Magnesium sulphate acts distinctly more strongly, which was to be expected of the bivalent kation in regard to the acid dyestuff, whereas by the trivalent aluminium the dyestuff had already been precipitated in the bath, before it could reach the fibre.

A second series gave the following result : (see table on next page).

So there were again distinct differences among univalent and among bivalent metals.

What is especially striking, is the fact that the stronger action depends upon the place of the metal in the potential series and not upon the atomic weight, as sodium not only extracts more than

lithium, which is lighter, but also zinc more than cadmium, which is heavier.

Salt.	Quantity in mg.	Quantity in mol.	Remarks.
Li_2 SO_4 1 aq.	60.5	$^1/_{2000}$	Colour of the bath decreases as indicated by arrow.
Na_2 SO_4 10 aq.	161.2	"	
Mg SO_4 7 aq.	123.3	"	
3 Cd SO_4 8 aq.	128.3	$^1/_{6000}$	Between Li and Na there is a clear difference.
Zn SO_4 7 aq.	143.8	$^1/_{2000}$	
Al_2 $(SO_4)_3$ 18 aq.	111.1	$^1/_{6000}$	Coagulation of the dyestuff in the bath; the fibre remains colourless.
Cr_2 $(SO_4)_3$ 18 aq.	65.4	"	
Fe_2 $(SO_4)_3$	85.5	"	

Magnesium seems to form an exception in this respect; however it turned out that this metal should not be compared with Zn and Cd, but with the alcaline earth metals, with which it shows more resemblance, also in other respects, than with zinc and cadmium.

Salt.	Quantity in mg.	Quantity in mol.	Remarks.
Hg Cl_2	135.6	$^1/_{2000}$	Colour of the bath decreases as indicated by the arrow.
Mg Cl_2 6 aq.	101.7		
Cd Cl_2 2 aq.	109.6		
Ca Cl_2 6 aq.	109.5		
Ba Cl_2 2 aq.	104.1		

From this survey we have conclusive evidence that magnesium belongs to the series $Mg < Ca < Ba$ of which it forms the least strong term, whereas cadmium must be considered to be one of the series $Hg < Cd < Zn$.

In both series the most electropositive metals are the most effective.

The series intersect and as magnesium is more electropositive than cadmium and zinc, and yet extracts less effectively, there must be another property beside electropositivity, which governs the extracting action of the metal.

II.

With a view to confirming the results communicated in the

preceding paragraph the investigation was extended and at the same time the estimation with the naked eye in the exhausted bath was replaced by a quantitative determination.

Instead of cotton-wool 1 gram skeins of cotton were used, which were first soaked in soapwater and then well rinsed. During 10′ at 65° they were brought into a bath of 1 milligram of carefully purified benzopurpurin 4B and different quantities of salt in 500 ccm. of distilled water.

After dyeing the bath was quickly cooled and compared with standard solutions of known concentration in a colorimeter of C. H. WOLF.

First of all we had to examine whether Behr's law was valid, *viz.* whether a cm. of a n. normal solution had the same intensity of colour as $p.a.$ cm. of a $^1/p$ n.normal solution, which in fact was the case.

It was necessary to use distilled water for the dilutions; water for drinking gave another shade to the field by which the sensiti veness was impaired.

For benzopurpurin and with solutions of, at the utmost, 1 milligram in 100 ccm., the sensitiveness of the method could be increased after some practice to 0.1 cm., at a thickness of the layer of 10 to 15 cm. *viz.* to less than one percent.

After this we had to examine the relation between the quantity of dyestuff, taken up by the cotton — using a fixed quantity of salt — and the concentration of the dyestuff.

Here one would expect a relation of the nature of the absorption equation.

However the quantity of dyestuff precipitated by the fibre appeared to be pretty much independent of the concentration of the dyestuff in the bath.

To that end respectively 1, $^1/_2$, $^1/_3$ and $^1/_4$ mgr. of benzopurpurin were dissolved in 100 ccm. H_2O containing 161,2 mgr. Na_2SO_4 10 aq. and in this sol. each time 1 gr. of cotton was dyed during 10′ at 65°; after that the exhausted bath was compared with the original solution (see table on next page).

It is to be expected that the independence just referred to will not hold good for higher concentrations of the dyestuff. As however it was our intention only to examine the influence of the electrolytes and as this effect became more lucid in this way, we confined our investigations in the beginning to concentrations of not more than 1 mgr. per 100 ccm.

Moreover with these small concentrations the colorimetric deter-

minations could be executed directly — without having to dilute.

Further it was shown that the quantity of dyestuff taken up depends on the concentration of the electrolyte, *however only to a*

Conc. of benzopurpurine.	Change of the intensity of colour.				Taken up by the fibre.
1 mgr.	15 cm. after dyeing	= 14 cm. orig. bath.			0.066 mgr.
$\frac{1}{2}$ „	„	= 13 „	„		0.066 „
$\frac{1}{3}$ „	„	= 12 „	„		0.066 „
$\frac{1}{4}$ „	„	= 11.1 „	„		0.065 „

certain limit; an increase of concentration *above* 10 millimol. in many cases does not cause a rise of the quantity of purpurin which is precipitated on the cotton.

A close investigation will have to decide whether this is due to a saturation of the cotton fibre with the electrolyte, by which a further rise of the conc. in the bath leaves the concentration in the fibre practically unchanged, in consequence of which the precipitating action cannot exceed a certain figure.

We shall not enter into further detail because this falls outside the scope of this communication.

A. Comparison of the action of $MgSO_4$ 7 aq, $(CdSO_4)_3 8H_2O$ and $Zn SO_4$ 7 aq.

Here several concentrations of the salts were used and for the rest the exhaustion of the bath (1 mg. purpurin per 500 ccm.) was defined as mentioned above. From this the quantity of dyestuff taken up by the cotton (1 gram; always at 65° during 10 minutes) was calculated by subtraction.

If, for example, it was found that a column of 15 cm. after dyeing had the same intensity of colour as 9.2 cm. before dyeing, then there was present in the bath $9.2/15 \times 100\%_0 = 61.5\%_0$ and hence the fibre had taken up $38.5\%_0$.

The determinations mentioned above were moreover controlled by comparing several of the exhausted solutions with each other.

So 15 cm. of the $ZnSO_4$ sol. of 0.25 millimol. should be equal to 14.5 cm. of the equimol. $MgSO_4$ sol.; 15 cm. of the $ZnSO_4$ sol. 0.33 millimol. = 13.4 cm. of the equimol. $CdSO_4$ sol. and = 13.2 cm. of the equimol. $MgSO_4$ sol. etc., which was always the case.

The observations contained in the scheme are for a part inserted in the graphic representation I.

$\mathcal{F}ig$ 1
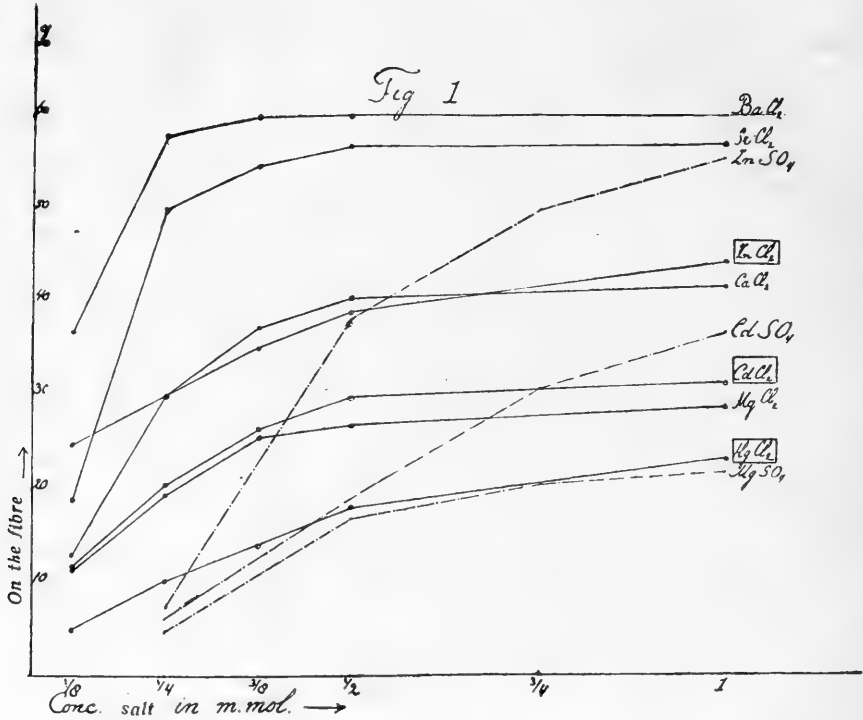
B. *Comparison of the action of the chlorides of Mg, Ca, Sr,*
Ba and of Zn, Cd and Hg.

As the concentration of these salts is not to be fixed accurately by weighing, standard solutions were made, the content of which was estimated by the VOLHARD volumetric method. These solutions were diluted to a content of 4 millimol. per 160 ccm. (284 mg. of chlorine).

Hence each ccm. contains $1/_{40}$ millimol.

To the bath of 1 mgr. of benzopurpurin in ± 0.5 litre of distilled water were now added respectively 5 ($1/_8$ millimol.), 10 ($1/_4$ millimol.), 15 ($3/_8$ millimol.), 20 ($1/_2$ millimol.) and 40 (one millimol.) ccm. of the different salt solutions and left in contact with 1 gram of cotton during 10 minutes at 65° as mentioned above.

Afterwards the exhausted baths were compared with the original dyestuff solution and in this way their strength was determined; by way of controlling the exhausted baths of different salts were also mutually compared and no deviations of any importance were ever observed.

The result of the investigation is given in table II and in diagram I.

Especially from the latter one observes immediately that the result

TABLE I.

Salt.	Quantity in mg.	Quantity in millimol.	Intensity of colour.	Taken up by the fibre.
Mg SO$_4$ 7 aq.	61.7	0.25	15 cm aft. dyeing $= 14.3$ before it	4.5 %
„	82.2	0.33	„ $= 13.4$ „	10.8 „
„	123.3	0.50	„ $= 12.5$ „	16.7 „
„	184.7	0.75	„ $= 11.9$ „	20.7 „
„	246.6	1.0	„ $= 11.7$ „	22.0 „
„	369.9	1.5	„ $= 11.2$ „	25.3 „
„	493.2	2.0	„ $= 11.0$ „	26.7 „
Zn SO$_4$ 7 aq.	71.9	0.25	15cm. aft. dyeing $= 13.8$ before it	7.5 %
„	95.9	0.33	„ $= 11.9$ „	20.7 „
„	143.8	0.50	„ $= 9.2$ „	38.5 „
„	215.7	0.75	„ $= 7.5$ „	50.0 „
„	287.6	1.0	„ $= 6.7$ „	55.3 „
„	431.4	1.5	„ $= 6.5$ „	56.7 „
„	575.2	2.0	„ $= 6.5$ „	56.7 „
$\frac{1}{3}$ { (Cd SO$_4$)$_3$ 8H$_2$0 }	64.1	0.25	15cm. aft. dyeing $= 14.1$ before it	6.0 %
„	85.5	0.33	„ $= 13.2$ „	12.0 „
„	128.3	0.5	„ $= 12.1$ „	19.0 „
„	192.4	0.75	„ $= 10.3$ „	31.3 „
„	256.6	1.0	„ $= 9.5$ „	37.7 „
„	384.9	1.5	„ $= 9.1$ „	39.3 „
„	513.2	2.0	„ $= 9.1$ „	39.3 „

of our preliminary observations has been entirely affirmed.

It is clear that magnesium in fact belongs to the group of the alcaline earth metals and that on the other hand zinc, cadmium, and mercury form a natural group.

Though the curves for calcium and zinc run closely beside one another, they bear no relation to each other in reality.

TABLE II.

Salt.	Conc. in millimol.	Intensity of colour.	Taken up by the fibre.
$MgCl_2$	1/8	15 cm. before dyeing = 13.3cm. after it.	11.3 %
$CaCl_2$	"	" = 13.1 "	12.9 "
$SrCl_2$	"	" = 12.1 "	18.8 "
$BaCl_2$	"	" = 9.5 "	36.7 "
$ZnCl_2$	"	" = 11.2 "	24.7 "
$CdCl_2$	"	" = 13.2 "	11.5 "
$HgCl_2$	"	" = 14.2 "	5.0 "
$MgCl_2$	1/4	15 cm. before dyeing = 12.1cm. after it.	19.5 %
$CaCl_2$	"	" = 10.5 "	30.0 "
$SrCl_2$	"	" = 7.5 "	50.0 "
$BaCl_2$	"	" = 6.3 "	58.0 "
$ZnCl_2$	"	" = 10.5 "	30.0 "
$CdCl_2$	"	" = 11.9 "	20.5 "
$HgCl_2$	"	" = 13.5 "	10.0 "
$MgCl_2$	3/8	15 cm. before dyeing = 11.2cm. after it.	25.5 %
$CaCl_2$	"	" = 9.4 "	37.5 "
$SrCl_2$	"	" = 6.8 "	54.5 "
$BaCl_2$	"	" = 6.0 "	60.0 "
$ZnCl_2$	"	" = 9.7 "	35.3 "
$CdCl_2$	"	" = 11.0 "	26.7 "
$HgCl_2$	"	" = 12.9 "	14.0 "
$MgCl_2$	1/2	15 cm. before dyeing = 10.9cm. after it.	26.7 %
$CaCl_2$	"	" = 8.9 "	40.7 "
$SrCl_2$	"	" = 6.5 "	56.7 "
$BaCl_2$	"	" = 6.0 "	60.0 "
$ZnCl_2$	"	" = 9.1 "	35.3 "
$CdCl_2$	"	" = 10.5 "	30.0 "
$HgCl_2$	"	" = 12.3 "	18.0 "
$MgCl_2$	1	15 cm. before dyeing = 10.6cm. after it.	29.3 %
$CaCl_2$	"	" = 8.7 "	42.0 "
$SrCl_2$	"	" = 6.5 "	56.7 "
$BaCl_2$	"	" = 6.0 "	60.0 "
$ZnCl_2$	"	" = 8.3 "	44.7 "
$CdCl_2$	"	" = 10.2 "	32.0 "
$HgCl_2$	"	" = 11.5 "	23.3 "

TABLE III.

Salt	Concentration in millimol.	Intensity of colour.	Taken up by the fibre.
MgCl₂	¼	15 cm. before dyeing = 14.4 cm. after it	4.0 %
CaCl₂	"	" = 11.0 "	26.7 "
SrCl₂	"	" = 10.0 "	33.0 "
BaCl₂	"	" = 9.0 "	40.0 "
. . . . .	. . . .	. . . .	. . . . .
ZnCl₂	"	" = 13.9 "	7.3 "
CdCl₂	"	" = 14.0 "	6.7 "
HgCl₂	"	" = 14.5 "	3.3 "
MgCl₂	½	15 cm. before dyeing = 13.3 cm. after it	11.3 %
CaCl₂	"	" = 8.5 "	43.3 "
SrCl₂	"	" = 7.9 "	47.3 "
BaCl₂	"	" = 7.2 "	52.0 "
. . . . .	. . . .	. . . .	. . . . .
ZnCl₂	"	" = 9.5 "	36.7 "
CdCl₂	"	" = 12.7 "	15.3 "
HgCl₂	"	" = 13.7 "	8.7 "
MgCl₂	¾	15 cm. before dyeing = 12.5 cm. after it	16.7 %
CaCl₂	"	" = 7.7 "	48.7 "
SrCl₂	"	" = 7.3 "	51.3 "
BaCl₂	"	" = 7.0 "	53.3 "
. . . . .	. . . .	. . . .	. . . . .
ZnCl₂	"	" = 8.2 "	45.3 "
CdCl₂	"	" = 12.1 "	19.3 "
HgCl₂	"	" = 13.3 "	11.3 "
MgCl₂	1	15 cm. before dyeing = 12.3 cm. after it	18.0 %
CaCl₂	"	" = 7.6 "	49.3 "
SrCl₂	"	" = 7.3 "	48.7 "
BaCl₂	"	" = 7.0 "	53.3 "
. . . . .	. . . .	. . . .	. . . . .
ZnCl₂	"	" = 8.1 "	46.0 "
CdCl₂	"	" = 11.5 "	23.3 "
HgCl₂	"	" = 13.3 "	11.3 "
As above	1 ½	Intensity of colour as with 1 millimol. of salt	Taken up by the fibre as with 1 millimol.

C. With a view to affirming the significance of this result we have examined the conduct of the self same series of salts towards a benzopurpurin solution 10 times more concentrated.

However here the quantitative estimation, used till now, could not be applied unmodified; the intensity of colour of the solutions was far too great to determine the differences by a simple comparison of the layers of the liquid.

Therefore we first tried to estimate the quantity of dyestuff by precipitation with potassium alum and weighing the precipitate; in doing this however fluctuating figures were obtained. Also the quantity of ash in these precipitates was too small to lead to an effective method.

The colorimetric method was now modified as follows: 10 ccm. of the exhausted bath were diluted to 100 ccm. and this solution was compared to one containing 1 mgr. of benzopurpurin in 500 ccm.

The concentrations found by comparison were now multiplied by ten in order to learn the conc. of the dyestuff in the exhausted liquid.

First we had convinced ourselves of the fact that, on diluting the solution of 10 mgr. in 500 ccm. to the tenfold volume a liquid was obtained, the intensity of which was equal to the standard solution (1 mgr.—500 ccm.), so that this method of dilution may be considered allowable. Table III gives a survey of the result obtained.

The character of the dyeing-curves is equal to that of the dye-bath diluted ten times; the succession of the metal salts has remained entirely the same. Now too we see magnesium join the group of the alcaline earths as the least pronounced representative. Striking but not strange is the relatively trifling action which it exercises, viz. it diverges remarkably from the Ca < Sr < Ba and so in that group it takes a somewhat isolated place. In the group of the bivalent heavy metals zinc also seems to stand somewhat apart by its relatively pronounced action.

D. With a view to the conformity between zinc and elements from the 7th and 8th group in their bivalent form, the conduct of manganese, iron, cobalt, and nickel was examined, to which end the sulphates were chosen. Here the difficulty presented itself that the salts of those metals had a colour of their own, so that a correction had to be applied. First it was made out that with the salt-concentrations used, so little of the salt itself was taken up by the fibre, that hereby no perceivable change of colour took place; this

of course was done without benzopurpurin being present in the bath.

Now, when a dye and a salt are present at the same time, probably more salt will penetrate the fibre; these quantities however were very small, as the ash content of the fibre material after dyeing did not amount to more than 3 milligrams.

The correction meant above consisted in this, that in the standard solution a quantity of salt was put equal to that of the exhausted dye-bath. It is true, by that the error was not quite avoided, because unequal layers of the liquids have to be compared; however, since

TABLE IV.

Salt.	Conc. in millimol.	Intensity of colour.	Quantity of dyestuff in the fibre.	
$FeSO_4$	$1/8$	15 cm. after dyeing $= 14.8$ cm. before it.	1	%
$MnSO_4$	"	" $= 13.9$ "	7.3	"
$CoSo_4$	"	" $= 11.5$ "	23.3	"
$NiSO_4$	"	" $= 10.5$ "	30.0	"
$FeSO_4$	$1/4$	15 cm. after dyeing $= 14.4$ cm. before it.	4.0	%
$MnSO_4$	"	" $= 13.2$ "	12.0	"
$CoSO_4$	"	" $= 10.6$ "	33.3	"
$NiSO_4$	"	" $= 9.3$ "	38.0	"
$FeSO_4$	$3/8$	15. cm. after dyeing $= 14.2$ cm. before it.	5.3	%
$MnSO_4$	"	" $= 13.0$ "	13.3	"
$CoSO_4$	"	" $= 9.5$ "	36.7	"
$NiSO_4$	"	" $= 8.5$ "	40.7	"
$FeSO_4$	$1/2$	15 cm. after dyeing $= 14.2$ cm. before it.	5.3	%
$MnSO_4$	"	" $= 12.9$ "	14.0	"
$CoSO_4$	"	" $= 9.2$ "	38.7	"
$NiSO_4$	"	" $= 8.5$ "	43.3	"
$FeSO_4$	1	15 cm. after dyeing $= 14.1$ cm. before it.	6.0	%
$MnSO_4$	"	" $= 12.9$ "	14.0	"
$CoSO_4$	"	" $= 9.2$ "	38.7	"
$NiSO_4$	"	" $= 8.0$ "	46.7	"

the intensity of colour of the very diluted salt solution is inconsiderable compared to that of the benzopurpurin, this error could be neglected.

The solutions of ferrous sulphate had to be prepared anew for each determination, because after some time, in consequence of oxidation, precipitation of ferric basic sulphate took place. As this was not entirely to be prevented the figures for this salt are given with some reserve, of the other salts standard solutions were made containing $1/_{40}$ millimol. per cent of which respectively 5, 10, 15, 20 and 40 cc. were used. For the rest we worked as is described under B p. 898 with the exception that a temperature of 70° was chosen.

First we see that zinc and also cadmium in some degree join these metals. Remarkable is the rapidly ascending course of the curve for zinc, a thing we had already found with zinc chloride in the concentrated solution of benzopurpurin. As yet we cannot decide whether this is based on accidental deviations or whether the higher temperature is the cause of it. As regards the metals of the iron group itself, we see that the precipitating faculty increases according to the atom number of the metals, except in the case of manganese; but the differences between manganese and iron are very small. We investigated also the *chlorides* of manganese, cobalt and nickel with which the same succession was found: Mn $<$ Co $<$ Ni with almost the same figures.

This result therefore agrees with what we found about the succession zinc, cadmium, mercury, *viz.* that the precipitating faculty is not connected directly with the atomic weight of the elements, but with a peculiar chemical property, for instance the electro affinity;
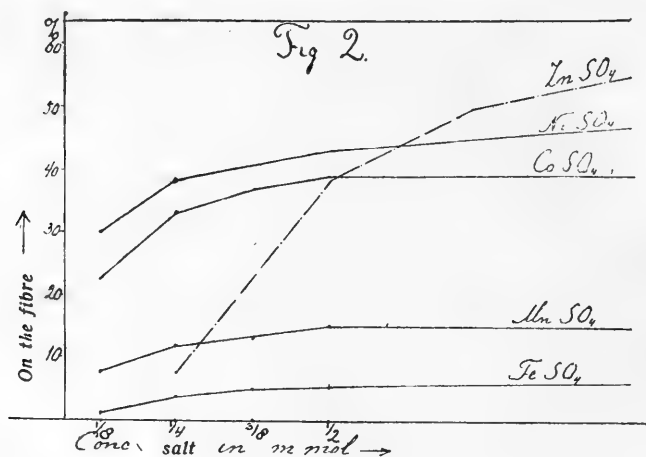
Fig 2.

but not exclusively with that either, because otherwise the action of zinc and magnesium could not be well understood (for the rest see fig. 2).

E. In the course of our preliminary experiments we had observed that lithiumsulphate exercised a smaller action than sodium sulphate; we have repeated these experiments in a quantitative way on the chlorides and supplemented them with NH_4Cl and KCl. Except those for lithium the figures are so near to each other that the deviations fall within the range of the experimental error.

Nevertheless we suppose the succession $Li < NH_4 < Na < K$ to be correct, in accordance with the increasing electro affinity (table V and fig. 3).

Fig 3.

I = LiCl.
II = NH₄Cl.
III = NaCl.
IV = KCl
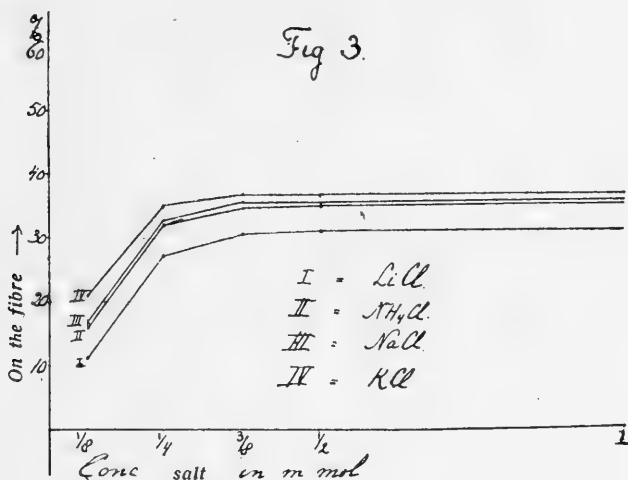
Also with the alcaline metals a limit was soon reached, which is situated at ± 33 °/₀, therefore considerably lower than that of the alcaline earths ($BaCl_2 = 60$ °/₀) and at about the same height as that of the other metals of the 2nd group, with the exception of mercury, manganese and iron, which are situated much lower.

With the fixation of the acid benzopurpurin we have kept our attention fixed on the metal. Because we were forced to examine some chlorides in order to obtain a survey of the alcaline earths, we were able to compare the action of a few chlorides with that of the sulphates.

Though the graphs indicate a shifting of the action towards lower concentrations, we did not in any case meet with essential differences, which was to be expected.

TABLE V.

Salt.	Conc. in millimol.	Intensity of colour.	Quantity of dyestuff in the fibre.
LiCl	$^1/_8$	15 cm. after dyeing = 13.3cm. before it.	11.3 %
NH₄Cl	„	„ = 12.6 „	16.0 „
NaCl	„	„ = 12.5 „	16.7 „
KCl	„	„ = 11.8 „	21.0 „
LiCl	$^1/_4$	15 cm. after dyeing = 10.8cm. before it.	27.5 %
NH₄Cl	„	„ = 10.2 „	32.0 „
NaCl	„	„ = 10.1 „	32.5 „
KCl	„	„ = 9.8 „	34.7 „
LiCl	$^1/_2$	15 cm. after dyeing = 10.4cm. before it.	30.7 %
NH₄Cl	„	„ = 9.8 „	35.0 „
NaCl	„	„ = 9.7 „	35.5 „
KCl	„	„ = 9.5 „	36.7 „
LiCl	$^3/_4$	15 cm. after dyeing = 10.3cm. before it.	31.3 %
NH₄Cl	„	„ = 9.8 „	35.0 „
NaCl	„	„ = 9.7 „	35.5 „
KCl	„	„ = 9.5 „	36.7 „
ditto.	1	Same figures as with $^3/_4$ millimol.	ditto.

The investigation will be continued in different directions, in the first place more attention will be directed to the influence of temperature.

November 1918.   *Organic Chem. Lab. of*
                                  the Technical University, Delft.

Chemistry. — *"The mutual influence on the electrolytic conductivity of gallic tannic acid and boric acid in connection with the composition of the tannins"*. By Prof. J. Böeseken and W. M. Deerns.

By the researches of Emil Fischer [1]) and others on the polydepsides, it is now very probable that the tannin of the gall-nut principally consists of a mixture of the pentadigalloylethers of α- and β-glucose, in which the two galloyl groups are coupled in such a manner that the carboxyl group of the one tannic acid molecule has been esterified with one of the OH groups in the meta position of the other tannic acid radical, thus:

$$\left[\begin{array}{c} HO \\ HO \langle \quad \rangle \; COO \langle \quad \rangle \; \begin{array}{c} COO \\ \end{array} \\ HO \qquad\qquad HO \quad OH \end{array} \right]_5 C_4H_7O$$
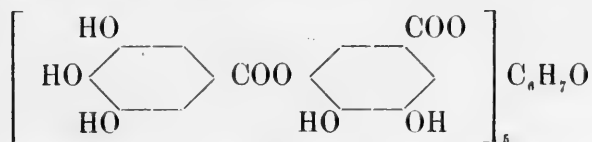
If this conception be the right one, then the influence of the conductivity of this substance on that of boric acid should be considerable, *viz.* should agree with that of five mol. pyrogallol + five mol. pyrocatachol per molecule of the tannin.

Here however two circumstances ought to be considered. In the first place a solution of the tannin, because of the high molecular weight (± 1700) has the character of a colloidal solution and *a priori* it is not certain that it will behave like an ordinary solution.

However a qualitative experiment showed that the increase of the conductivity was considerable, so that *the solution of the tannin behaved quite normally as regards that phenomenon.*

In the second place the tannin must not be compared with pyrogallol and pyrocatechol, but with the esters of gallic acid and of protocatechuic acid.

Therefore we have first measured the influence, which the conductivity of the gallic acid methylester exercises on that of boric acid.

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[1]) Berichte **45**, 915 (1912).

Increase of conductivity of a 0.5 mol. H_3BO_3 solution at 25° in
KOHLRAUSCH-HOLBORN-units $\times$ 10[6].

Conc.	Pyrocatechol.	Pyrogallol.	Gallic acid.	Gallic acid methyl ester.	Tannin of the gallic acid
$^1/_{16}$ m.	137.2	136.2	61.8	—	—
$^1/_{32}$ „	88.3	103.3	27.9	212.5	
$^1/_{64}$ „			11.1	137.8	
$^1/_{128}$ „			1.5	89.5	
$^1/_{256}$ „			−9.3	53.1	
$^1/_{512}$ „			−13.5	30.7	
$^1/_{1024}$ „			−14		

This influence proved to be very great.

We had expected it to be greater than that of gallic acid. From the researches on free acids it was proved that here two influences are making themselves felt; the first is the eventually increasing influence of boric acid on the substances; the second is the *decreasing* influence of boric acid as *a medium* on the conductivity of the acids.

With an acid of the strength of gallic acid this decreasing influence is rather important; the dissociation constant is equal to $\pm 4 \times 10^{-5}$, so it is situated between that of glutaric and adipic acid.

From this one may fix approximately the decreasing action of different dilutions in percentages of the original conductivity [1]).

Acid.	$K^{25} \times 10^5$	$^1/_{24}$ mol.	$^1/_{48}$ mol.	$^1/_{96}$ mol.	$^1/_{192}$ mol.
Glutaric acid.	4.71	12.5	13.8	17.1?	21.2
Gallic acid.	4.00	12.7	(14.—)?	(17.—)	21.7
Adipic acid.	3.26	12.9	12.1?	17.0	22.3

Instead of the increases of the conductivity which were found, one calculates the figures mentioned below, *viz.* one obtains figures entirely of the same order as those fixed for pyrogallol and pyrocatechol; they are distinctly higher even and approach those of gallic acid methyl ester. From this one may draw the conclusion that the carboxyl group in the benzine nucleus exercises an *increasing* influence on the rise of the conductivity caused by pairs of hydroxyl

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[1]) Recueil **36**, 177 (1917).

groups, favourably situated in regard to each other; this appears *directly* if the acid H is substituted by methyl, but may be indirectly deduced when the negative influence of the medium (boric acid) on the conductivity of the free acid is taken into account.

Dilution.	Found.	After correction
16	61.8	173
32	27.9	125
64	11.1	97
128	1.5	83

After having acquired these data the influence on the conductivity of boric acid → tannic acid was measured.

To this end tannin of the gall-nut was used (as the only tannin available at the present moment) which we prepared according to E. FISCHER and FREUDENBERG (loc. cit.) and from which *free* gallic acid was eliminated as well as possible.

Supposing the molecular weight to be 1700, the following figures could be deduced from the measurements. (Conductivity of a 0,5 mol. $H_2Bo_3 = 27 \times 10^{-6}$ K.H. units).

Dilution.	Innate conductivity	Conductivity $+0.5$ m H_3BO_3.	λTannin $H_3BO_3 - (\lambda$Tannin$ + \lambda H_3BO_3)$
213	91.6	350	+ 230.3
426	57.1	229	143.8
852	35.5	153	89.4
1704	21.8	105	55.1

From these figures we see that the increase of the conductivity is *very considerable*; in a dilution 213 even it is markedly higher than that of the gallic acid methyl ester in the dilution 32. So the molecule of the gallic tannic acid forms a complex boric acid compound, many times stronger than that of the gallic acid methyl ester, which already heightens the acidity so strongly.

This result in the first place entirely agrees with the structure of this tannin fixed by E. FISCHER, there are 10 *pairs* of favourably situated hydroxyl groups in every molecule.

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In the second place it is of importance because we learn to understand the very intense action of boric acid on the vegetable organism; it stands to reason that small quantities of this substance must exercise a considerable influence if it is able to turn the very common tannins from almost neutral substances into strong acids.

Org. Chem. Lab. of the Technical University.

Delft, November 1918.

Physics. — "*Magnetic properties of cubic lattices.*" By Prof. L. S. ORNSTEIN and Dr. F. ZERNIKE. (Communicated by Prof. H. A. LORENTZ.)

(Communicated in the meeting of September 29, 1918).

The well-known model of EWING has been treated more in detail by different scientists. A few have taken the very unsatisfactory standpoint, that elementary magnets are distributed at random in space [1]). More in accordance with reality is the supposition, from which W. PEDDIE [2]), and later on also HONDA and OKUBA [3]) have started, that the magnetic particles are arranged in a cubic lattice. The reasonings however show two important fallacies.

In the first place they neglected the demagnetising force in a sphere; accordingly they .think that dipoles cannot yield a result, which made them unnecessarily consider magnets of finite length. In the second place they considered only those rotations at the research of stability, in which the magnetic axes of all particles are moved in mutual parallelism.

As will be shown hereafter, the consequence of this unfounded limitation in the freedom of motion of the particles is that the stability becomes much greater than is in reality the case.

If we sweep this limitation, we find that the arrangement of magnetic atoms in a cubic lattice is unstable without exterior field. A body of such a structure, can therefore possess no coërcitive force.

§ 1. We consider a cubic lattice with edge d. In the corners of the lattices we imagine dipoles possessing the strength p, and which can rotate freely. Be those dipoles directed all parallel to an edge of the lattice by a strong exterior field H. Now we put the question how far the exterior of the field must be weakened to reach the limit of stability. If the system without exterior field is stable the intensity H_g at which this is the case, will be negative.

The magnetic properties of the lattice considered will consequently

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[1]) GANS u. HERTZ, Zeitsch. für Mathematik und Physik.

[2]) Edinburgh Proc. 195 and 7.

[3]) Phys. Review, X, 1917, p. 705.

— if H_g is negative — be roughly speaking analogous with those of a ferro-magnetic body with hysteresis. If on the contrary we find a positive value for H_g, we have to do with a body without hysteresis that can only be magnetised up to saturation by a strong field H_g. With a weaker exterior field the magnetic atoms will not remain totally directed and consequently M will decrease. We shall deduce for that case the connection between the intensity H and magnetisation, in other words: the permeability.

In order to find from H_g the coërcitive force H_c, we must bear in mind that the latter is defined as the negative *interior* field required to make the magnetisation change its sign. This interior field will always be found by adding the field H_{con}, which is caused by the magnetised body itself, to the exterior field H_e. The field H_{con} must be calculated on the supposition, that the body has a continuous space-magnetisation.

So we have

$$H = H_e + H_{con} \text{ and especially } H_c = - H_g - H_{con}.$$

Here — H_{con} is the so-called demagnetising force. By this definition H_c will become independent of the form of the body considered, which consequently is not the case for H_g. In the preceding paragraph we must consequently read for H_g everywhere $H_g + H_{con}$. In our calculation we shall always take the limit spherical. Then H_{con} is $- \frac{1}{3} M$.

It is easy to demonstrate that H_g becomes $= 0$ when we impose on the turning of the atoms the limitation discussed above that their axes always remain parallel. For this purpose we only have to sum up the reciprocal energy of two dipoles over the whole lattice. From considerations of symmetry we then find that this sum is zero. [1])

We shall give another proof of the theorem mentioned, the principle of which can also be useful for our further calculation.

We choose a system of axes parallel with the edge of the lattice and take the origin in one of its points. We imagine in all the points of the lattice except in the origin, Northpoles of unity strength, and we imagine the lattice limited by a very large sphere about 0. Let $V_0(x,y,z)$ represent the potential in a point x,y,z. The potential of dipoles with moment p in de x-direction is $p \dfrac{\partial V_0}{\partial x}$,

the intensity in 0 is consequently $p \dfrac{\partial^2 V_0}{\partial x^2}$, $p \dfrac{\partial^2 V_0}{\partial y \partial x}$, $p \dfrac{\partial^2 V_0}{\partial z \partial x}$ respectively in the x, y and z-direction. The potential energy of a dipole

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[1]) H. A. LORENTZ, Theory of Electrons. Note 55, p. 208.

with moment p' in 0 will consequently be $pp' \dfrac{\partial^2 V_0}{\partial x^2}$, when this dipole was also directed along the x-axis, whilst it amounts to $-pp' \dfrac{\partial^2 V_0}{\partial y \partial x}$, when the last dispole is directed along the axis of y.

When we place in all corners equally directed dipoles, we can dissolve these in dipoles according to the direction of the axes in components with moments p_x, p_y, p_z. And so the potential energy of the dipole in the origin is:

$$-\left\{ p^2_x \frac{\partial^2 V_0}{\partial x^2} + p^2_y \frac{\partial^2 V_0}{\partial y^2} + p^2_z \frac{\partial^2 V_0}{\partial z^2} + 2p_x p_y \frac{\partial^2 V_0}{\partial x \partial y} + \right.$$

$$\left. + 2p_x p_z \frac{\partial^2 V_0}{\partial x \partial z} + 2p_z py \frac{\partial^2 V_0}{\partial z \partial y} \right\} ..$$

On account of the symmetry the three mixed differential-quotients are zero, and we have further $\dfrac{\partial^2 V_0}{\partial x^2} = \dfrac{\partial^2 V_0}{\partial y^2} = \dfrac{\partial^2 V_0}{\partial z^2}$. Consequently these differential-quotients are also zero because V_0 fulfills the equation of LAPLACE. In consequence therefore the interior energy of the lattice is zero, independent of the direction of the dipoles (provided all dipoles are parallel). So a very weak exterior field will be sufficient to let all dipoles assume the directions of this field, in other words: H_q is zero.

The same result holds good for the two other BRAVAIS cubic arrangements: the centred cubic and the plane-centred cubic lattice. The limitation used thus yields a coercitive force which is equal to one third of the magnetisation of saturation. For steel the coercitive force is at least 80 times smaller.

2. In what follows we shall want the potential V of a rectangular lattice with unequal edges a, b, and c for the case that every corner carries a pole of unity strength; this potential depends upon the form of the boundary even if we imagine it at great distance. We shall avoid the difficulties of the boundary by the following artifice. Besides the point-charges 1 in the corners we give the body a homogeneous space-charge of -1 per volume a, b, c. In total the body is thus uncharged and the parts at a great distance of the particle considered have a vanishing influence. So we are able to calculate the potential V' for this case of a lattice infinitely extended in all directions. From this we shall then find V for the case of a sphere by adding the potential in a homogeneous sphere with a charge-

density $+\dfrac{1}{abc}$, which with exception of a constant is equal to $-$

$$\dfrac{x^2 + y^2 + z^2}{6abc}.$$

We begin by calculating the potential U, which is caused by the charges lying between the planes $z = \pm \frac{1}{2} c$. Evidently U is a periodical function of x and y with the periods a and b. So it may be represented by a double series of FOURIER:

$$U = \Sigma \, Z_{mn} \, \cos \dfrac{2\pi m}{a} x \, \cos \dfrac{2\pi n}{b} y \qquad \begin{array}{l} m = 0, 1, 2 \dots \\ n = 0, 1, 2 \dots \end{array},$$

in which for the sake of symmetry only the cosinus appears. The coefficients Z_{mn} are functions of z, which can be determined from the equations:

$$\Delta U = \dfrac{1}{abc} \quad \text{for} \quad |z| < \tfrac{1}{2}c \qquad \Delta U = 0 \quad \text{for} \quad |z| > \tfrac{1}{2}c$$

with the conditions of limit

$$U_{z = \pm \infty} = 0 \quad \left(\dfrac{\partial U}{\partial z}\right)_1 = \left(\dfrac{\partial U}{\partial z}\right)_2, \quad \text{for} \quad z = \pm \tfrac{1}{2}c.$$

Now the FOURIER-series for $z \neq 0$ may be twice differentiated, so that after substitution in these equations every term separately must fulfill the homogeneous equations, and Z_{00} the equation $\Delta Z_{00} = \dfrac{1}{abc}$. From this we shall find

$$Z_{00} = \begin{array}{ll} 0 & |z| > \tfrac{1}{2}c \\[2mm] \dfrac{(\frac{1}{2}c - |z|)^2}{2abc} & |z| < \tfrac{1}{2}c \end{array} \qquad Z_{mn} = B_{mn} \, e^{-l|z|} \qquad l = 2\pi \sqrt{\dfrac{m^2}{a^2} + \dfrac{n^2}{b^2}}$$

In order to determine still B_{mn} we can take $z = 0$ and use the ordinary form of coefficients:

$$\dfrac{ab}{4} B_{mn} = \int_0^a dx \int_0^b dy \; U_{z=0} \cos \dfrac{2\pi m}{a} x \cos \dfrac{2\pi n}{b} y$$

in which when m or n are zero we must have $\dfrac{ab}{2}$. For $U_{z=0}$ we have

$$U_{z=0} = \Sigma \Sigma_{i \; k} \left(\dfrac{1}{4\pi r_{ik}} + C_{ik}\right)$$

in which r_{ik} is the distance to the point (ia, kb) and C_{ik} the potential of the parallelepipedum abc with that point as centre, homogeneously filled. For the sake of convergence we shall here for a moment

introduce $r^{-1} e^{-rz}$ as law of attraction and in the result take $\varepsilon = 0$. Then we can write

$$U_{z=0}(\varepsilon) = C(\varepsilon) + \sum_i \sum_k \frac{e^{-\varepsilon r_{ik}}}{4\pi r_{ik}},$$

where $C(\varepsilon)$ is the potential of the infinite space homogeneously filled, and thus is a constant, only dependent on ε.

If we substitute the values of $U(\varepsilon)$ in the double integral, the term $C(\varepsilon)$ will consequently yield zero. In the other term the sum and the integration may be interchanged. The various integrals may then be united into a single one over all rectangles. And so we obtain:

$$\iint\limits_{-\infty}^{\infty} \frac{\cos \dfrac{2\pi m}{a} x \, \cos \dfrac{2\pi n}{b} y}{4\pi \sqrt{x^2 + y^2}} e^{-\varepsilon\sqrt{x^2+y^2}} \, dx \, dy.$$

By introducing pole-coordinates this integral may be reduced to

$$\frac{1}{2\pi} \int\limits_0^\infty dr e^{-\varepsilon r} \int\limits_0^\pi \cos(lr \sin q) \, d\varphi = \tfrac{1}{2} \int\limits_0^\infty J_0(lr) e^{-\varepsilon r} dr = \frac{1}{2\sqrt{l^2 + \varepsilon^2}}$$

and thus for $\varepsilon = 0$

$$\frac{ab}{4} B_{mn} = \frac{1}{2l}.$$

The potential found can further easily be summed up for all the layers of distance c in which the lattice may be divided by planes perpendicularly to the z-axis. In a point for which $0 < z < \tfrac{1}{2}c$ all layers under the point yield

$$\frac{(\tfrac{1}{2}c - z)^2}{2abc} + \Sigma B_{mn} \{e^{-lz} + e^{-l(z+c)} + e^{-l(z+2c)} + \ldots\} \cos \frac{2\pi m}{a} x \, \cos \frac{2\pi n}{b} y =$$

$$= \frac{(\tfrac{1}{2}c - z)^2}{2abc} + \Sigma B_{mn} \frac{e^{-lz}}{1 - e^{-lc}} \cos \frac{2\pi m}{a} x \, \cos \frac{2\pi n}{b} y$$

and all planes above it

$$\Sigma B_{mn} \frac{e^{-l(c-z)}}{1 - e^{-lc}} \cos \frac{2\pi m}{a} x \, \cos \frac{2\pi n}{b} y$$

so

$$V' = \frac{(\tfrac{1}{2}c - z)^2}{2abc} + \Sigma \frac{2}{abl} \frac{e^{-lz} + e^{-l(c-z)}}{1 - e^{-lc}} \cos \frac{2\pi m}{a} x \, \cos \frac{2\pi n}{b} y . \quad . \quad (1)$$

in which the sign Σ' means, that we must take half of the terms for which $m = 0$ or $n = 0$, whilst there is no term for $m = n = 0$.

For the spherically limited lattice without space-charge we ultimately find

$$V = -\frac{x^2+y^2+z^2}{6abc} - \frac{(\frac{1}{2}c-z)^2}{2abc} + S \quad . \quad . \quad . \quad . \quad (2)$$

where S represents the series Σ' of (1).

Formula (1) evidently holds good for $0 < z < c$.

From the potential V determined in this way we can find as above the potential energy of a dipole with the components p'_x, p'_y, p'_z, when the latter is placed in a point (x, y, z) of the field caused by dipoles p_x, p_y, p_z in the corners of the lattice.

The expressions

$$- \left(p_x p'_x \frac{\partial^2 V}{\partial x^2} + \ldots + (p_x p'_y + p_y p'_x) \frac{\partial^2 V}{\partial x \partial y} + \ldots \right)$$

will represent this energy.

From (2) follows for the derivatives of second order occurring in this expression

$$\frac{\partial^2 V}{\partial x^2} = \frac{\partial^2 S}{\partial x^2} - \frac{1}{3abc} \quad , \quad \frac{\partial^2 V}{\partial y^2} = \frac{\partial^2 S}{\partial y^2} - \frac{1}{3abc} \quad ,$$

$$\frac{\partial^2 V}{\partial z^2} = \frac{\partial^2 S}{\partial z^2} + \frac{2}{3abc} \quad , \quad \frac{\partial^2 V}{\partial y \partial z} = \frac{\partial^2 S}{\partial y \partial z} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

3. In order to examine generally the stability of the system described in (2), we must study the behaviour of the quadric form, representing the potential energy as function of the variables determining the direction of all dipoles. The difficulty of this problem does not lie so much in the great number of variables, as in the impossibility to form a single series, in which the variables relating to neighbouring magnets, follow each other closely.

This difficulty does not present itself in the case when there are dipoles placed on one line at mutually equal distances. There the stability may easily be examined in the well-known fashion with the help of a determinant. We shall mention a few of the results, as they may guide us in the case that has our attention. If all magnets are directed by a field parallel to the line, the system is still stable if the field is abolished. If we apply a slowly increasing field, contrary to the magnetisation, there may be indicated a definite group of small deviations of the dipoles, for which the system first becomes unstable. These displacements are such that the magnets lie in one plane and alternately will make angles $+ \varphi$ and $- \varphi$ with the direction of the field. The coercitive force found for this displacement of the magnets is only one third of the force found from the supposition, that all magnets turn parallelly.

For the case of the cubic lattice the analogous general method is impracticable for the reason mentioned above, but it is clear that also there we must find the combination of deviations, which most easily leads to an unstable position of the magnets. This combination must serve in calculating the coercitive-force, and it will yield for this quantity a smaller value than all other virtual displacements. Led by the analogy of the above mentioned simple case we shall examine those combinations of displacements, in which the dipoles of the lattice are distributed over two equal groups, which show an opposite displacement. Further it will be favourable in order to get unstability if the magnets with opposite deviations are placed as alternately as possible.

We can obtain a division into two groups by starting from a plane through three arbitrarily chosen points of the lattice and then using the system of parallel planes which contains all points. The dipoles lying in such planes can be assigned in a systematic way to each of the groups. The most obvious method is to count the planes alternately to the first and to the second group. Let the chosen planes divide the three edges of the elementary cube, respectively in l, m, and n parts. The dipoles on the x-axis will belong alternately to the two groups, when l is odd, but all to the same group if l is even. From this it follows that in principle there are possible only three divisions into groups i. e. dipoles along three, along two or only along one axis belonging alternately to different groups. These divisions can be obtained by starting respectively from the octahedron, the rhomb-dodecahedron or the cube-plane.

In the same way we can examine the distribution of the points of the central cubic lattice, by paying attention to the question whether the dipoles lying on three of the cube-diagonals belong or do not belong to different groups. Here the two last cases appear to be identical. Consequently there are only two possibilities, which belong respectively to the octaeder and the rhomb.-dodecahedron plane. When we consider the distributions of the plane-centred cubic lattice we can take three diagonals in the sides which meet in one corner. Then the first and the third case are identical and belong to the octahedron-plane, the second case belongs to the cube-plane.

With each of the lattices mentioned we meet with a way of the deviations that will yield no sharper criterion for the stability than the deviation in parallel of all dipoles. These are the distributions that belong to the octahedron-plane. For it is evident that for each half separately the equivalency of the three directions of axes still exists. Analogous to what has been discussed sub 1 it

holds good not only for each part separately, but also for the parts mutually, that the energy is zero for every position of the dipoles. The coercitive-force thus becomes again a third of the magnetisation of saturation, for other divisions into two groups a much smaller, even a negative value being found.

There are still many other divisions into groups conceivable, which perhaps may be of interest when another direction of the exterior field is chosen. So e. g. the division into three groups. In the case exclusively treated here where the field is parallel to the edge of the cube, they appeared to yield a greater value for H_e than that calculated below.

4. We shall take the y-axis in the direction of the exterior field, the x- and z-axes along the two other edges. For an arbitrary division into two halves the dipoles of which are directed parallel to the xy-plane, and form angles $+ \varphi$ and $- \varphi$ with the y-axis, we can indicate the energy as follows. Every dipole may be decomposed into a y-component $p \cos \varphi$ and an x-component $p \sin \varphi$ for the one and $- p \sin \varphi$ for the other group. The y-components form a complete cubic lattice and their mutual energy is consequently zero. In consequence of the exterior field H_e each dipole has an energy $p H_e \cos \varphi$ and so the dipoles together an energy of $\dfrac{p}{d^3} H_e \cos \varphi$ per unity of volume. Also the magnetical energy of the x-dipoles and the y-dipoles is zero on account of the cubic arrangement of these latter. The mutual energy of all x-components thus remains to be calculated. In order to determine this we imagine the x-components of the dipoles of the second group inversed in sign.

Then all are directed in the same way and their mutual energy is zero. If now we inverse the dipoles again then only the mutual energy of the two groups becomes different in sign. The energy sought for of all dipoles together is thus equal to twice the mutual energy of the two groups. We shall now calculate this with the help of (2).

Call the potential caused by unit-poles placed in the first half V, then the energy of a magnet with moment $- p \sin \varphi$ in the field of the first group the dipoles of which have a moment $p \sin \varphi$ is according to what preceded

$$p^2 \sin^2 \varphi \, \frac{\partial^2 V}{\partial x^2}$$

or per unity of volume

$$\frac{p^2}{2 d^3} \sin^2 \varphi \, \frac{\partial^2 V}{\partial x^2}.$$

The total energy per volume-unity is thus for the system

$$-\frac{p}{d^3} H_e \cos \varphi + \frac{p^2}{d^3} \frac{\partial^2 V}{\partial x^2} \sin^2 \varphi . \quad . \quad . \quad . \quad . \quad (4)$$

The second derivative with respect to φ of this expression is for $\varphi = 0$

$$\frac{p}{d^3} H_e + \frac{2p^2}{d^3} \frac{\partial^2 V}{\partial x^2}$$

The energy is a minimum and the equilibrium stable as long as it is positive.

For the limiting case we have

$$H_g = -2p \frac{\partial^2 V}{\partial x^2} .$$

And consequently the coercitive force becomes

$$H_c = \frac{p}{3d^3} + 2p \frac{\partial^2 V}{\partial x^2} = 2p \frac{\partial^2 S}{\partial x^2} . \quad . \quad . \quad . \quad . \quad (5)$$

the last according to (3), where $abc = 2d^3$.

When this formula yields a negative value a positive field stronger than $-- H_c$ is necessary to make the position $\varphi = 0$ stable.

For a weaker field we find the equilibrium-positive from the first derivative of (3)

$$H \sin \varphi + 2p \frac{\partial^2 V}{\partial x^2} \sin \varphi \cos \varphi = 0$$

or

$$\cos \varphi = -H / 2p \frac{\partial^2 V}{\partial x^2}$$

The magnetisation is here $I = \dfrac{p \cos \varphi}{d^3} = -\dfrac{1}{2d^3 \dfrac{\partial^2 V}{\partial x^2}} H = \beta$. The

magnetic field within the sphere is $U - \frac{1}{3} I = U (1 - \frac{1}{3} \beta)$ and the inductive $U + I = U (1 + \beta)$. The constant permeability of the matter is consequently

$$\mu = \frac{1+\beta}{1-\frac{1}{3}\beta} = \frac{\dfrac{d^3 H_c}{p} + \frac{2}{3}}{\dfrac{d^3 H_c}{p} - \frac{1}{3}} .$$

For the divisions into two groups, which we have discussed sub 3 we can always calculate $\dfrac{\partial^2 V}{\partial x^2}$ according to the series found in 2 and the relation (2), where in some cases we must turn the x and z axis

over an angle of 45° or interchange the x, y and z axis. The series always show strong convergence; for the following numbers, the calculation of 8 terms was only necessary in one case.

The table given below gives the values calculated for H_c in this way. For the cases in which the lattice is unstable, the permeability is indicated in the unstable direction. In the third to the fifth column the values of a b and c used in the calculation are mentioned.

Lattice	Varying planes	$\dfrac{a}{d}$	$\dfrac{b}{d}$	$\dfrac{s}{d}=\dfrac{c}{2d}$	$\dfrac{H_c}{M}$	μ
Cubic	111				$^1/_3$	
	010	1	1	1	$+1.104$	
					-0.0521	14
					-0.0521	14
	011	1	$\sqrt{2}$	$^1/_2\sqrt{2}$	$+0.546$	
					$+0.546$	
					-0.0925	3.2
Centred cubic	111				$^1/_3$	
	011	1	$\sqrt{2}$	$^1/_2\sqrt{2}$	$+0.440$	
					$+0.440$	
					$+0.1209$	
Face centred cubic	111				$^1/_3$	
	001	$^1/_2\sqrt{2}$	$^1/_2\sqrt{2}$	$^1/_2$	$+0.668$	
					$+0.1610$	
					$+0.1610$	

We must remark, that for the three cases always occurring with equal values of a, b and c only one calculation was necessary. For we can interpret them as belonging to one and the same division in two groups, but with the exterior field successively in the three directions of the axes. According to (5) the values of H_c belonging to it will taken together be equal to $\dfrac{p}{a^3} = M$. Moreover on account of symmetry only two are always equal to each other, so that only one must be calculated. The smallest value of H_c for each lattice is printed in bold type, the others have importance mainly for the

calculation. So the centred and the plane-centred show coercitive force, and even in a degree much too great for steel e.g.

In all our considerations we have left unconsidered the heat-movement. The magnetic properties found here are apparently always represented by magnetisation-curves consisting of straight lines. These broken straight lines will no doubt be rounded off by the heat-movement, and consequently resemble more those under observation. Another cause for the rounding off must be looked for in the fact that the real materials are aggregates of crystals lying at random in all directions. For the present we draw the attention for the effect of this cause to the well-known theories of PIERRE WEISS.

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Utrecht.
Groningen, } September 1918.

Physics. — *"On the theory of the Brownian motion."* By Prof. L. S. Ornstein and Dr. H. C. Burger. (Communicated by Prof. H. A. Lorentz).

Prof. van der Waals Jr. has developed in these communications[1]) a new theory of the Brownian motion. We shall demonstrate in this paper, that he has made use of various wrong suppositions and theses in his reasoning.

1. Van der Waals starts from the equation of motion of a Brownian particle in the formula:

$$\ddot{x} = w(t) \quad \dots \quad \dots \quad (1)$$

Here $w(t)$ is the force which the particle experiences from the molecules of the liquid. The force $w(t)$ is a magnitude depending upon chance.

In order to arrive at a theory of the Brownian motion v. d. Waals introduced the supposition that $\dot{x}_0 w(t)$ — the product of the velocity at the time zero and the force at the time t — is zero "on an average over all particles[2]).

Now we can understand the average in two ways, viz.:

a. at a given initial velocity x_0, thus $\overline{w(\vartheta)} = 0$.

b. at all possible initial velocities, in which case the distribution of velocity according to Maxwell must be taken into consideration. Van der Waals uses the average in the way last mentioned. We shall also examine to what the supposition leads if we apply the first way of determining the average and show that the determination according to (a) as well as v. d. Waals uses it leads to impossible consequences.

In this purpose we take down the first integral of (1), which is

$$\dot{x} = \dot{x}_0 + \int_0^t w(\vartheta)\, d\vartheta \quad \dots \quad \dots \quad (2)$$

If we determine the average according to (a) we obtain

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[1]) These com. Vol. XX. 1918. p. 1254.

[2]) cf. p. 1258 of the paper quoted.

$$\overline{\dot{x}} = \dot{x}_0,$$

which in physics is an impossible result.

If we square (2) and determine the average according to (a), we obtain

$$\overline{\dot{x}^2} = \dot{x}_0^2 + \overline{\left\{ \int_0^t w(\vartheta) \, d\vartheta \right\}^2}$$

a result which, as is immediately obvious, is opposed to the theorem of equipartition, as the average of the second member is essentially positive, so that if e.g. x_0^2 is more than the equipartition-value, this would also be the case with $\overline{\dot{x}^2}$. If we determine the average of the square of (2) in the supposition (b) we find

$$\overline{\dot{x}^2} = \overline{\dot{x}_0^2} + \overline{\left\{ \int_0^t w(\vartheta) \, d\vartheta \right\}^2}$$

And as now $\overline{x_0^2}$ in this case has the equipartition-value, $\overline{\dot{x}^2}$ would be essentially more than this value, which contains a contradiction, as the average square of the velocity must be equal for all particles, at any moment.

VAN DER WAALS has made use of the second integral of (1) viz.

$$x = x_0 + \dot{x}_0 t + \int_0^t w(\vartheta) \, (t - \vartheta) \, d\vartheta$$

to arrive at his theory. In the same way as above we can demonstrate that this combined with his supposition $\overline{\dot{x}_0 w(t)} = 0$ leads to incorrect results, contrary to theory and observation. For if we make up $\overline{x - x_0} = \overline{\Delta^2}$, supposition (a) yields

$$\overline{\Delta^2} = \dot{x}_0^2 t^2 + \overline{\left\{ \int_0^t w(\vartheta) \, (t - \vartheta) \, d\vartheta \right\}^2}.$$

And as the average in the second member is positive the highest power of t which occurs in $\overline{\Delta^2}$ will as least be 2, consequently v. D. WAALS' supposition comes into conflict with the formula $\overline{\Delta^2} = bt$, which he applies himself (p. 1257 l.c.). If we determine the average according to (b) the only difference is that x_0^2 must be replaced by the equipartition value of the velocity-square, so that also in determining the average according to VAN DER WAALS the formula used by him combined with his supposition $\overline{\dot{x}_0 w(t)} = 0$ leads to an incor-

rect result. Besides the negative conclusion that the theory of v. D. WAALS ought to' be rejected some positive result can be deduced from our calculations.

The formula (1) is just as much a matter of course as it is right [1]) and consequently there must be a mistake in the supposition $\overline{\dot{x}_0 w(t)} = 0$, while there can be no difficulty for anyone in seeing that everything is all right when this magnitude can become negative for fixed values of t. We shall in this paragraph use the average according to (a). As $\dot{x}_0$ has been given once and for all, the above reasoning shows, that $\overline{w(t)}$ for certain values of t must possess the opposite sign of $\dot{x}_0$ [2]). Now VAN DER WAALS has rightly drawn attention to it, that according to statistical mechanics for $t = 0$, $\overline{w(t)} = 0$. Besides it is evident, that for t infinite the average value of $w(t)$ undergoes no influence from $\dot{x}_0$ and therefore must be zero. The course of $w(t)$ may consequently be imagined in a way as represented by the accompanying figure (where $\dot{x}_0$ has been supposed positive).
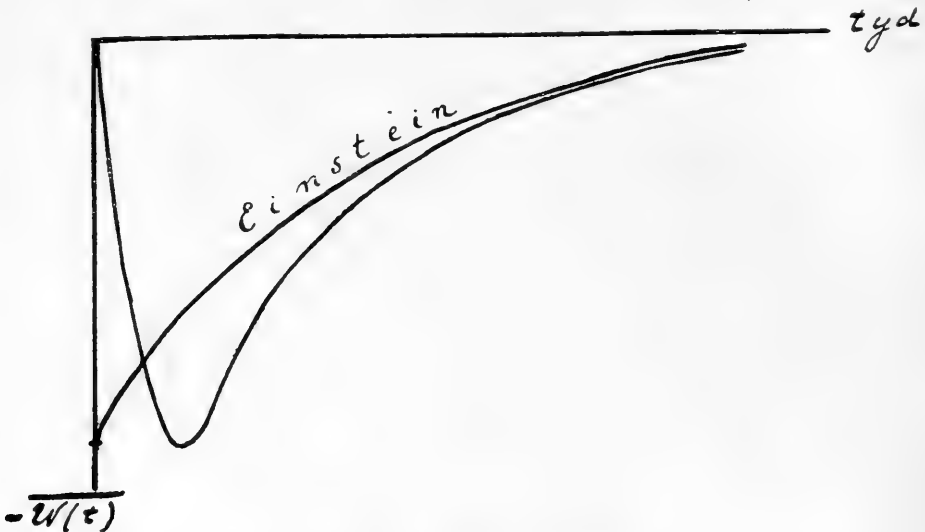
Of course the curve may be more complicated for example $\overline{w(t)}$ might oscillate round the axis. If now we calculate $\overline{w(t)}$ according to the EINSTEIN-LANGEVIN formula, we find, if we take into consideration that $\overline{F(t)}$ is equal to zero:

$$w(t) = -\overline{\beta \dot{x} + F(t)} = -\beta e^{-\beta t}\, \dot{x}_0$$

[1]) From the formula (1) we can deduce the relation $\overline{\Delta^2} = bl$ if we introduce suppositions, it is however impossible to find the value of b, without penetrating into the mechanism of the Brownian motion.

[2]) There are cases, when this is not so necessary according to what precedes, but if $\dot{x}_0$ is more than the equipartition value, it is certainly the case.

For $t = 0$ the line, which represents this course, deviates from the true curve. The important agreement existing between EINSTEIN's theory and the experiment now makes us presume, that the true $w(t) - t$ curve and the curve according to EINSTEIN only deviate from each other for short times after the departure of the particle with the velocity $\dot{x}_0$, that so the maximum in the true curve lies close to $t = 0$, and that from this maximum onward it descends pretty well exponentially according to EINSTEIN's curve. It goes without saying that these are only assumptions, which a calculation of the true $\overline{w(t)}$ curve must prove from the molecular theory. We are however of opinion that it is worth while to point to this possible interpretation of EINSTEIN's master-stroke in the theory of the Brownian motion.

§ 2. VAN DER WAALS' theory further rests on the thesis that the magnitude

$$w(t) \overline{\int_0^t w(\vartheta) (t - \vartheta) d\vartheta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is essentially negative, if only t be not taken to small.

Perhaps it is not quite superfluous to demonstrate after what precedes, that this thesis is not right; expecially as an integral of the same kind used by one of us may be treated in the same way [1]).

When $w(t)$ is a function determined by chance, of which the character is not dependent upon the time, we can represent it for a long interval by a FOURIER-series, the coëfficients of the FOURIER-series determine the nature of the accidental character [2]). If so

$$w(t) = \Sigma_n \left(A_n \sin \frac{2\pi n t}{T} + B_n \cos \frac{2\pi n}{T} t \right),$$

when $w(t) = 0$, we must have $B_0 = 0$.

The calculation of (3) becomes simple, when we apply that

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[1]) Compare L. S. ORNSTEIN. On the Brownian motion. These Proc. XXV, 1917. p. 96.

[2]) When we have to do with a function of accidental character, even then the conduct of this function may very well depend upon the time. If we consider e.g. the length of the path in Brownian motion, we get for all times $\Delta = 0$, but $\overline{\Delta^2} = bt$, for the velocity however we have $\overline{v} = 0$. $\overline{v^2}$ is constantly independent of the time. For the force something analogeous as for the velocity ought to be assumed. By going further into the mechanism of the motion, this can be rendered plausible.

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$$\int_0^t w(\vartheta)\,(t-\vartheta)\,d\vartheta = \int_0^t dt \int_0^t w(\vartheta)\,d\vartheta$$

or as the zero point of the time is arbitrary, it may be replaced by

$$\int_\varsigma^{t+\varsigma} w(\vartheta)\,(t+\xi+\vartheta)\,d\vartheta = \int_0^t dt \int_\varsigma^{t+\xi} w(\vartheta)\,d\vartheta.$$

The average value in question may now be represented by

$$\overline{w(t)\int_0^t w(\vartheta)\,(t-\vartheta)\,d\vartheta} = \frac{1}{T}\int_0^T d\xi\, w(\xi+t)\int_0^t dt \int_\varsigma^{t+\varsigma} w(\vartheta)\,d\vartheta.$$

For the sake of simplification the time-unity may be chosen so that the time T is equal to 2π, thus we find

$$\int_\xi^{\xi+t} w(\vartheta)\,d\vartheta = \sum_n \left[-\frac{A_n}{n}\{\cos n(t+\xi) - \cos n\,\varsigma\} + \frac{B_n}{n}\{\sin n(t+\xi) - \sin n\xi\} \right]$$

which once again integrated with respect to t from o to t yields

$$\sum_n \left[-\frac{A_n}{n^2}\{\sin n(t+\xi) - \sin n\xi\} + \right.$$

$$\left. + \frac{A_n}{n}\, t\cos n\xi - \frac{B_n}{n^2}\{\cos n(t+\xi) - \cos n\xi\} - \frac{B_n}{n}\, t\sin n\xi \right].$$

This expression must subsequently be multiplied by

$$w(t+\xi) = \sum_n \{A_n \sin n\,(t+\xi) + B_n \cos n(t+\xi)\}$$

and thus integrated with respect to ξ from zero to 2π. Then all terms of the product in which n has odd values fall out. At last the average value sought for is given by

$$\overline{w(t)\int_0^t w(\vartheta)\,(t-\vartheta)\,d\vartheta} = \frac{1}{2\pi}\sum \left(-\frac{C^2{}_n}{n} + \frac{C^2{}_n}{2n^2}\cos nt + \frac{C^2{}_n}{2n}\, t\sin nt \right)$$

where $C_n^2 = A_n^2 + B_n^2$. In the usual way this sum may be converted into an integral, in which the average value $\dfrac{C_n^2}{2\pi}$ is represented by $f(n)$[1]. In the average value described we find in this way

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[1] By PLANCK, EINSTEIN, LAUE series of FOURIER have been applied in the discussion of questions of probability (e.g. average values).

$$\int_0^\infty \frac{f(n)}{2n^3} (nt \sin nt + \cos nt - 1)\, dn\,{}^1).$$

The sign of this integral may for larger values of t be made quite arbitrarily by proper choice of $f(n)$. That it should be essentially negative is consequently not true [2]).

3. In the quoted paper by ORNSTEIN the first theory of the Brownian motion as developed by Dr. SNETHLAGE and J. D. v. D. WAALS was criticised on the basis of the fact that it comes into conflict with the theorem of equipartion.

There the thesis was made use of that

$$\left\{ \overline{\int_0^t w(\xi) \sin \varrho\,(t-\xi)\, d\xi} \right\}^2 . \quad\quad\quad\quad (5)$$

is proportional to t. Here $w(\xi)$ is a function subjected to chance, so that the average value is zero [3]). In a note VAN DER WAALS says: "This change of sign (of $w(\theta)\,w(\theta+\delta)$) was overlooked by ORNSTEIN. In consequence of this he arrived at the remarkable conclusion, that it is not allowed to accept that $\frac{d}{dt}\overline{u^2} = 0$. For from this it follows according to his calculation that $\overline{u^2}$ is not constant, but the sum of a lineary and periodical function of t!"

It is necessary to remark in contradiction to this, that the differential equation [4]) of v. D. WAALS—SNETHLAGE viz.

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[1]) For $t = \infty$ this expression becomes equal to $\frac{t}{4} f(0)$, is thus essentially positive (i.e. f is essentially positive).

For very great values of t we can require that the average is $\varphi(t)$, then we get

$$\frac{f(n)}{n} = \frac{2}{\pi} \int_0^\infty \frac{\varphi(\lambda)}{\lambda} \sin n\lambda\, d\lambda$$

for very small values of t the average value is also positive.

[2]) The proof that v. D. WAALS gives of the disputed thesis by differentiating $\overline{\Delta^2}$ (p. 1331 of his paper) is not right. The formula $\overline{\Delta^2} = bt$ is deduced by a transition to a limit, and the process is such that in differentiating $\overline{\angle^2}$ we do not get b as $\triangle$ cannot be differentiated.

[3]) Compare ORNSTEIN, these reports XXI, p. 96.

[4]) The equation, which is treated by both authors as a differential equation, does not apply, as they suppose, to arbitrary kinds, but only to the commencement of the movement, compare ORNSTEIN and ZERNIKE, These Proc. XXI, p. 109.

$$\frac{d^2u}{dt^2} = -\varrho^2 u + w \qquad \bar{w} = 0 \text{ (given ad } \dot{u}_\circ \text{ and } u_\circ)$$

eads to incorrect results. For we get according to their equation

$$\bar{u}^2 = \left(u_\circ \cos \varrho t + \frac{\dot{u}_\circ}{\varrho} \sin \varrho t \right)^2 + \frac{1}{\varrho^2} \left\{ \int_0^t w(\xi) \sin \varrho(t-\xi) \, d\xi \right\}^2$$

and as we shall once again prove further on the last average value is proportional to t. From the suppositions of VAN DER WAALS and Miss SNETHLAGE the remarkable conclusion does really follow, that the velocity of a Brownian particle should increase infinitely.

The proof of the thesis that (5) is proportional to t, which is only slightly different from a deduction given by PLANCK already in another connection, runs as follows. The integral may be written in the form:

$$\int_0^t \int_0^t \overline{W(\xi) \, W(\eta)} \sin \varrho \, (t-\xi) \sin \varrho(t-\eta) \, d\xi \, dy.$$

or if we interchange integrating and determining the average :

$$\int_0^t \int_0^t \overline{W(\xi) \, W(\eta)} \sin \varrho(t-\xi) \sin \varrho(t-\eta) \, d\xi \, d\eta.$$

If now we introduce $\eta = \xi + \psi$, we get

$$\int_0^t d\xi \sin \varrho(t-)\xi \int_{-\xi}^{t-\xi} \overline{W(\xi) \, W(\xi+\psi)} \sin \varrho(t-\xi-\psi) \, d\psi$$

In this form we again introduce for W a FOURIER-series in which $\overline{W}_\circ = 0$, whilst we must take $B = 0$.

We then find for the average value

$$\overline{W(\xi) \, W(\xi+\psi)} = \underset{n}{\Sigma} (A^2{}_n + B^2{}_n) \cos \frac{2\pi}{T} n\psi$$

So that the integral in question if for the sake of simplification we take $\frac{2\pi n}{T} = \varrho_n$ becomes

$$\int_0^t \sin \varrho \, (t-\xi) d\xi \int_{-\xi}^{t-\xi} \underset{n}{\Sigma} (A_n{}^2 + B_n{}^2) \sin \varrho \, (t-\xi-\psi) \cos \varrho_n \psi \, d\psi =$$

$$= \Sigma (A_n{}^2 + B_n{}^2) \int_0^t \sin \varrho(t-\xi) d\xi \int_{-\xi}^{t-\xi} \sin \varrho(t-\xi-\psi) \cos \varrho_n \psi \, d\psi.$$

While calculating these integrals we need only take into account terms, which get the highest power of $\varrho - \varrho_n$ in the denominator, as only these contribute in a way worth mentioning to the result. If we execute the quite elementary calculation we arrive at the result

$$\left\{ \overline{\int_0^t W(\xi)\, \sin \varrho(t-\xi)\, d\xi} \right\}^1 = \sum_n \frac{\sin^2 \dfrac{\varrho-\varrho_n}{2} t}{(\varrho-\varrho_n)^2}\, (A_n{}^2 + B_n{}^2)$$

When ϱt is great we can write for this

$$(A^2 + B^2) \int_0^\infty \frac{\sin^2 \dfrac{\varrho-\varrho_n}{2} t}{(\varrho - \varrho_n)^2}\, d\varrho_n = (A^2 + B^2)\, \frac{t\pi}{4}\ ;$$

in which A and B are the coefficients of the terms of the series for which $\varrho_n = \varrho$, consequently $\dfrac{2\pi n}{T} = \varrho$, or rather the integer that lies closest to this.

As long as $A^2 + B^2$ differs from zero the value of the average in question is proportional to the time. $A^2 + B^2$ is *strictly* zero, this does not hold good, but there is not a single reason to suppose, that in the Brownian motion the term of which the frequency is determined by ϱ should just be missing in the FOURIER-series. But even should it be missing, we should on the basis of the suppositions of VAN DER WAALS and Dr. SNETHLAGE arrive at the improbable result, that the average value of the velocity of a Brownian particle never reaches the equipartiton value.

4. In VAN DER WAALS' paper it is urged that LANGEVIN's deduction of the formula $\overline{\Delta^2}$ would contain an inner inconsistency. This inconsistency is held not to appear in the theory that Mrs. Dr. DE HAAS-LORENTZ has worked out on the basis of EINSTEIN's formula. And as the starting point according to EINSTEIN and that of LANGEVIN are identical, it would be surprising if the one theory would be inwardly inconsistent and the other not, unless LANGEVIN should have made a blunder in calculation. This however is not the case; if we formulate the basis as was done in ORNSTEIN's paper, there exists no contradiction. As well EINSTEIN's theory as that of LANGEVIN rests on the following suppositions

$$\frac{du}{dt} = -wu + F \ . \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6a)$$

$$\overline{F} = 0 \quad \ldots \quad \ldots \quad \ldots \quad (6\beta)$$

$$\int_{-\infty}^{+\infty} \overline{F(\xi)\,F(\xi+\psi)}\,d\psi = \frac{kT}{m}\beta = \vartheta. \quad \ldots \quad (6\gamma)$$

provided we start from particles which at the time $t = 0$, have the velocity u_0.

If we accept this set of equations, which kinetically have not been proved, which however contains the inconsistency developed in § 1, we *afterwards* do not arrive at any contradiction.

Van der Waals looked for it in the equation arising when (2) is multiplied by u and the average is determined, he wrote down [1])

$$\overline{u\frac{du}{dt}} = -\overline{wu^3}$$

which is really incorrect, but he forgot then that $\overline{Fu}$ is not zero, if we put ourselves on the standpoint of the suppositions $6(\alpha, \beta, \gamma)$; as Ornstein demonstrated on p. 1011 of his paper. If we introduce for $\overline{uF}$ the value found there the equation adopts the form

$$\overline{u\frac{du}{dt}} = \beta\left(u_0{}^2 - \frac{\vartheta}{2\beta}\right)e^{-2\beta t}$$

For times large with reference to $\dfrac{1}{\beta}$ this is zero, whilst if the average is determined over all particles it is always zero as $\overline{u_0{}^2} = \dfrac{\vartheta}{2\beta}$.

Now it is supposed in Langevin's proof that $\overline{xF} = 0$. It might be doubted perhaps whether this magnitude is equal to zero [2]). Yet this is the case. For we have

$$\frac{d^2x}{dt^2} = -\beta\frac{dx}{dt} + F$$

so

$$x = x_0 + \frac{u_0}{\beta}(1-e^{-\beta t}) + \int_0^t e^{-\beta\xi}\,d\xi\int_0^\xi e^{\beta\eta}\,F(\eta)\,dy$$

so

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[1]) Langevin has not developed any reasonings that could give rise to the supposition that he puts $\overline{Fu} = 0$.

[2]) On the fact that $\overline{xF} = 0$ rests the very simple theory which Langevin gave of the Brownian motion.

$$\overline{F\dot{x}} = [x_0 + \frac{u_0}{\beta}(1 - e^{-\beta t})]\,\overline{F} + F\int_0^{\overline{\xi}} e^{-\beta\zeta}\,d\xi\int_0^{\xi} e^{\beta\eta}\,F(\eta)dy$$

The first term is zero according to 6β, for the second term we can write by partial integration

$$-\frac{1}{\beta}\overline{F(t)e^{-\beta t}\int_0^t e^{\beta\eta}F(\eta)\,dy} - \overline{F'(t)\int_0^t F(\eta)\,dy}.$$

The two last integrals are equal, as $F'(t)\,F(\eta)$ is different from zero only if η lies in the immediate neighbourhood of t. The value of both integrals, as proved in ORNSTEIN's paper, is $\dfrac{\dot{\vartheta}}{2}$.

Thus it becomes clear that there is no question of inner contradiction, and that only the supposition about $W(t)$ — incorrect through the times of commencement — is an error in the theory of EINSTEIN and LANGEVIN. As we showed in § 1 of this paper the value which according to EINSTEIN's formula is obtained for the average force at a given velocity at the time zero $\overline{W(t)}$ only deviates for a very short time from the real value of this magnitude. The fact that EINSTEIN's formula leads to results which agree well with reality support the supposition that the relation

$$\overline{W(t)} = -\beta\dot{x}_0\,e^{-\beta t}$$

holds with a very good approximation already a very short time after the moment in which all emulsion-particles possess the velocity $\dot{x}_0$. The true kinetic theory of the Brownian motion will perhaps be able to give an account of this fact.

Institute for Theoretical Physics.

Utrecht, Sept. **1918.**

Physics. — *"The audion as an amplifier."* By G. HOLST and E. OOSTERHUIS. (Communicated by Prof. H. A. LORENTZ.)

(Communicated in the meeting of October 26, 1918).

In a recently published article G. VALLAURI [1]) communicated some calculations about the audion as an amplifier. He points out, that under normal conditions, one may approximately represent the anode current of the audion I as a lineair function of the grid potential v and the plate potential V:

$$I = av + bV + c.$$

If in the plate circuit a resistance R is placed, it may be easily calculated that the variations of the current I_v in the plate circuit depend upon the variations v_v of the grid potential in the following way:

$$I_v = \frac{a}{1 + bR}\, v_v.$$

Now VALLAURI takes the ratio $\dfrac{I_v}{v_v}$ as a measure for the amplification. It appears to us that more satisfactory results are obtained, if we do not assume $\dfrac{I_v}{v_v}$ as the amplification, but the dimensionless ratio of the potential variations on the resistance R to the variations of the grid potential. The amplification then becomes $G = \dfrac{aR}{1 + bR}$ and for large values of R: $G_{max} = \dfrac{a}{b}$.

If instead of a resistance a selfinduction L is placed in the anode circuit, we get, if the frequency of the grid variations is n:

$$G = \frac{\text{variation potential on selfinduction}}{\text{variation grid potential}} = \frac{2\pi n La}{\sqrt{1 + 4\pi^2 n^2 b^2 L^2}},$$

and for large values of L: $G_{max} = \dfrac{a}{b}$.

In the case of a capacity C connected in parallel to the self-induction L we obtain:

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1) Nuovo Cimento (13) 169, 1917.

$$G = \frac{2\pi \, n \, La}{\sqrt{(1 - 4\pi^2 n^2 \, LC)^2 + 4\pi^2 \, n^2 \, b^2 \, L^2}}.$$

G now becomes a maximum for $4\pi^2 n^2 \, LC = 1$, i.e. if the circuit (LC) is tuned to the grid potential frequency [1]).

We again find $G_{max} = \dfrac{a}{b}$.

The amplification as defined above, has the same maximum value $\dfrac{a}{b}$ in any case, so that it indicates a property of the audion. That our definition is an obvious one, is readily seen in the case one has to do with several audions connected in series. The tension on the resistance or self-induction in the anode circuit of the first audion is connected to the grid of the second and so on. The ratio of the variations in the grid potentials of the two audions is therefore equal to G, and so will be the ratio of the anode current variations. This latter ratio can easily be measured. Indeed we found the maximum ratio of the anode current variations to be equal to $\dfrac{a}{b}$.

2. In order to increase the amplifying action of the audion,
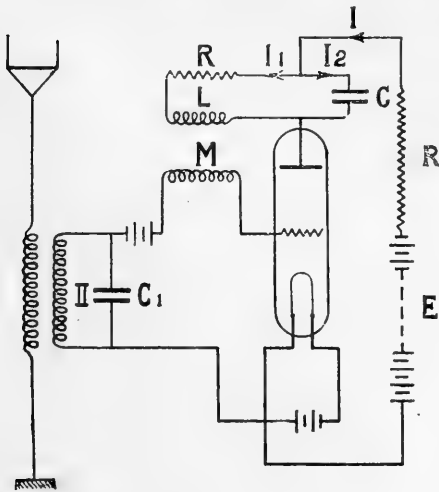
FRANKLIN among others have advised the use of reaction circuits, in which the plate current reacts on the grid circuit, e.g. by magnetic coupling.

We will discuss now, the characteristic properties of the audion that are of importance in reaction circuits and more specially in the case of figure 1.[2])

We have assumed that in the secondary circuit a damped vibration is set up, and that the potential on the condensor C_1 is of the form

$$v = f(t) = w \sin 2\pi \, nt \, (1 - e^{-\rho t}) \, e^{-\sigma t}$$

In this case we get the following system of equations

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[1]) While in the two previously treated cases, large values of R and L must be used to obtain maximum amplification, here normal L and C will suffice.

[2]) See VALLAURI loc. cit. fig. 7.

$$I = av + bV + c \qquad\qquad I = I_1 + I_2$$

$$W - RI_1 - L\frac{dI_1}{dt} = 0 \qquad\qquad v = f(t) - M\frac{dI_1}{dt}$$

$$W - \frac{1}{C}\int I_2\, dt = 0 \qquad\qquad V = E - R'I - W.$$

Here W is the potential on the condensor C and M the coefficient of mutual induction of the reaction coil.

From these equations a differential equation for W may be derived

$$\alpha\frac{d^2 W}{dt^2} - \beta\frac{dW}{dt} + \gamma W = \delta + Raf(t) + Laf'(t).$$

where

$$\alpha = CL(1 + bR')$$
$$\beta = CR(1 + bR') + bL + aM.$$
$$\gamma = 1 + b(R + R')$$
$$\delta = R(c + bE).$$

The solution of this equation is of the form

$$W = \frac{\delta}{\gamma} + e^{-\frac{\beta}{2\alpha}t}\; P\sin\left(\frac{\sqrt{4a\,\gamma - \beta^2}}{2\alpha}t + \varphi\right)$$
$$+ e^{-\sigma t}\, aw\, A\sin(2\pi\, nt + \chi)$$
$$- e^{-(\varrho+\sigma)t}\, aw\, B\sin(2\pi\, nt + \psi).$$

If the circuit (LRC) is tuned to the incoming oscillations $\sqrt{4\alpha\gamma - \beta^2} = 4\imath\, n\alpha$. Putting the damping factor $\dfrac{\beta}{2\alpha} = D$ we find for the variable part of W an expression of the form:

$$W_v = aw\,\frac{4\pi^2\, n^2 + D^2}{1 + b(R + R')}\left\{ \begin{array}{ll} e^{-Dt} & F\sin(2\pi\, nt + \xi) \\ + e^{-\sigma t} & G\sin(2\pi\, nt + \eta) \\ - e^{-(\varrho+\sigma)t} & H\sin(2\pi\, nt + \zeta) \end{array} \right\}$$

in which F, G and H are functions of σ, ϱ, L, R and D only.

The first four quantities are independent of the audion, the last one D however is a function of a and b, but by varying the coefficient of mutual induction M of the reaction coil any value of D may be obtained, so that independent of a and b the most effective damping can always be obtained.

So we come to the conclusion, that in a reaction circuit, when R and R' are not extraordinarily large, W_v is proportional to a and independent of the value $\dfrac{a}{b}$, which gave the maximum amplification in the previously treated cases.

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Mathematics. — *"Remark on the plane translation theorem"*. By Prof. L. E. J. Brouwer.

The *plane translation theorem* enunciated by me in Vol. XII of these Proceedings (p. 297) and completely proved for the first time in Vol. 72 of the Mathematische Annalen (p. 37—54), runs as follows:

A continuous one-one transformation of the Cartesian plane Γ in itself with invariant indicatrix, but without an invariant point, is a translation all over the plane.

We mean by this that each point of Γ is situated in a *translation field*, i. e. in a region lying outside its image region and bounded by two simple open lines not meeting each other, one of which is the image of the other.

Let t be the given transformation, T a translation field belonging to t, $_nT$ for each positive or negative integer n including zero the image of T for the transformation t^n. The set of points $T' = \underset{n}{\mathfrak{S}}\,(_nT)$ can be represented binniformly and continuously on a Cartesian plane C in such a way that the image of the transformation t of T' is a translation of C. Thus, *if by a convenient choice of T we can arrange T' to fill up the whole plane Γ, Γ can be represented biuniformly and continuously on a Cartesian plane C in such a way that the image of the transformation t of Γ is a translation of C.*

However the question, *whether for each transformation t a choice of T making T' to fill up the whole plane Γ, is possible*, must be answered in the negative, as was indicated by me in a footnote on page 37 of the quoted paper of the Mathematische Annalen, and as appears from the following example:

In Γ we define a Euclidean system of measurement, and a rectangular system of coordinates founded on it. The straight lines $y = 1$ and $y = -1$ divide Γ into three regions $g_1\,(y>1), g_2\,(1>y>-1)$, and $g_3\,(y<-1)$. Each of the regions g_1 and g_3 we fill up with a pencil of lines $y = c$, and the region g_2 we fill up with a pencil of lines $y^2 = \dfrac{x-c}{1+x-c}$. These three pencils together with the lines $y = 1$ and $y = -1$ form a pencil β of simple open lines not intersecting each other, and covering Γ entirely.

We shall now understand by t the transformation carrying each point P of Γ on the line of β passing through it along an arc of constant length l: *to the left*, if P lies in g_1 or on the boundary of g_1; *upward*, if P lies in g_2; *to the right*, if P lies in g_3 or on the boundary of g_3. This transformation t is duly biuniform and continuous, has no invariant point, and leaves the indicatrix invariant. But if for each positive or negative integer n including zero we represent the image of P for the transformation t^n by $_nP$ and $\mathfrak{S}(_nP)$ by P', P' *does not depend on P continuously* (for, if the sequence of points $P_1, P_2, P_3, \ldots$ lying in g_2 converges to the point P lying on the line $y = -1$, the sequence $P_1', P_2', P_3', \ldots$ does not converge exclusively to P', but also to other points of Γ).

Thus neither can Γ be represented biuniformly and continuously on a Cartesian plane C in such a way that the image of the transformation t of Γ is a translation of C. For, if such a representation were possible, P' would necessarily depend on P continuously.

Physiology. — *"A new ophthalmoscope"*. By Prof. J. K. A. Wertheim Salomonson.

In a former communication made at the meeting on April 27th 1917 I showed a collection of photographs of the living human retina. I described and exhibited two different photographic ophthalmoscopes, the second of which has been in regular use and gives satisfactory results. As a matter of fact we can also use it for simply showing a retina to any person not familiar with ophthalmoscopy, as the instrument can be easily adjusted in exactly the right position before the eye to be examined, the observer only having to focus the image. But if an instrument of this kind has to be used solely for demonstrating purposes a thorough reconstruction including many modifications might prove judicious. In that case we ought to provide for the possibility of using several different magnifications, which in the case of the photographic instrument, giving a real image of 40 millimetres in diameter would have been irksome. With the photographic instrument the ocular magnification amounted to 3.5 times, corresponding to an absolute enlargement of the fundus of about 15 diameters.

In the second place we should have to discard the arclamp the light of which for our purpose can only practically be dimmed by absorbing light-filters.

We might have substituted for the small screens used for intercepting the light reflected by the ophthalmoscope lens some more appropriate means, at least if photography were not intended.

Lastly it should be possible to materially reduce the dimensions of the whole apparatus, rendering it more easy to handle.

Starting from these considerations, I have built an entirely new instrument, to be used solely for viewing the retina and showing it to students as yet unskilled in the art of ophthalmoscopy.

The principle of indirect ophthalmoscopy has been applied as was also the case with the photographic instrument. For illumination a small 25-candle power gas-filled lamp with a straight tungsten filament-spiral was used, normally burning on a 4-cell accumulator or on a small alternating current transformer for 8 Volts secondary.

The light intensity is generally reduced with a sliding contact variable resistance.

A condensor projects the image of the filament on a narrow slit. A lens placed on the slit projects the condensor aperture on the
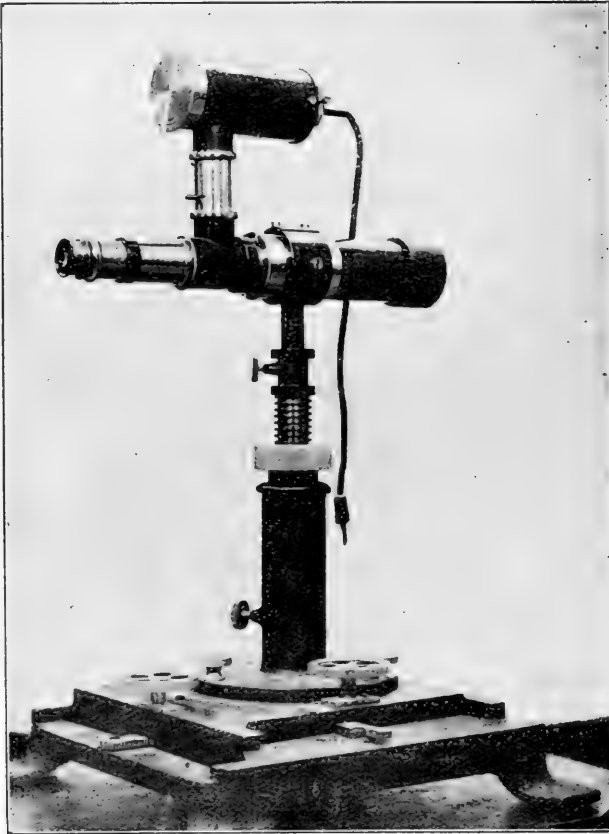
ophthalmoscope lens, the light being deflected 90 degrees by a small totally reflecting prism placed beneath the slit, so as to permit of placing the illuminating tube at a right angle to the axis of the viewing tube, containing the ophthalmoscope lens. The real image of the retina, formed by the ophthalmoscopelens can be examined through an aperture beneath the prism. We inspect that image with a kind of short microscope, the objective of which has a focal distance of 55 millimeters, the eye piece being one of the Huygenian type as used in the ordinary microscope. The magnification is altered on the use of different eyepieces.

In order to eliminate the images reflected by the ophthalmoscope lens, the following arrangement is used. A small achromatic double

image prism of calcspar and glass is placed between the condensor and the slit and causes two images of the filament to be projected in the plane of the slit. Only one of these, formed by the ordinary rays falls in the slit, the other falls on one of the slitplates and is arrested. Consequently the eye is illuminated with polarised light and the images reflected by the ophthalmoscope lens are also polarised. By means of a nicol prism placed in the microscope tube these reflexes are extinguished. The light illuminating the retina and reflected from the fundus of the eye has become depolarised and can be observed with the microscope. As a matter of fact the retina is clearly seen without any appreciable disturbing reflexes from the surface of the intervening media. Also the retinalreflexes, which in young patients are nearly always very noticeable, seem to be very slightly lessened.

The construction of this ophthalmoscope appears to possess some advantages. According to the HELMHOLTZ-GULLSTRAND theory we use one small part of the pupil in the patient's eye for transmitting the illuminating light-cone, whereas another part of the pupil takes up the narrowest part of the double cone of rays emerging from the retina and passing into the eye of the observer. These cones should be entirely separated by a narrow unused zone both of the cornea and of the anterior and posterior surface of the lens. Only in this way is it possible to prevent the occurrence of reflexes emerging from these surfaces which pass into the eye of the observer and disturb the ophthalmoscopic image by diffused light from the substance of the cornea and the lens. With my instrument the reflexes can never reach the observer as they would also be obscured by the nicol prism. Therefore we have only to consider the light diffused by the illuminated parts of cornea and lens. The lens is in this respect more troublesome than the cornea, especially in young individuals, whereas in adult patients both show nearly the same opalescence. Consequently we might in some cases — at least theoretically — lessen the distance between the illuminating and observation cone of light, and we should be able to examine eyes with narrow pupils — at least smaller ones with our instrument than with other instruments of the same kind. The reason that I have adjusted the instrument without considering this possibility may be found in the fact that I wished to have an instrument which would be ready for use with any patient without any adjustment except of course the final focussing.

With this instrument we can see at once 27° of the fundus of an emmetrope eye, corresponding to about 4¹/₂ diameters of the papilla

nervi optici. The whole field is remarkably flat, and sharp up to the edges. The magnification is generally about **14** diameters, or about the same as when the eye is examined with the direct method, but with an angle of view many times greater. By using stronger
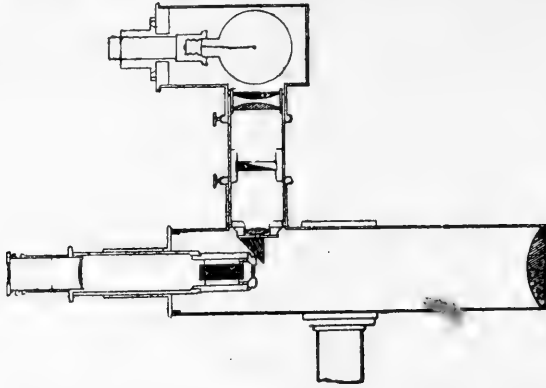
eyepieces the image, which is in the upright position, can be magnified up to about 50 times, the angle of view of course being somewhat reduced. As the illuminating filament can be regulated to any desired degree of brightness we can even with this high magnification get a profusion of light, and exceedingly clear and sharply defined images of the fundus.

When in use the distance from the patient's eye to the instrument is about **90** millimeters. The only change necessary when examining different patients, is the focussing. In cases of strongly myopic, hypermetropic or astigmatic eyes, examination is still possible with the patient wearing his own glasses.

The ophthalmoscope lens in this instrument is one of the well-known aspheric aplanatic single lenses of **43** mm. clear aperture, made by ZEISS. One might use any other aplanatic combination of lenses, provided the focal distance and aperture were satisfactory. The multiple reflexes from a combination of lenses would be obscured as effectually as those from a single lens.

Physiology. — *"Tonus and faradic tetanus"*. By Prof. J. K. A. WERT-
HEIM SALOMONSON and Mrs. RATU LANGI— HOUTMAN.

If a muscle be stimulated with the secondary current of an
induction apparatus fitted with a vibrating interrupter we generally
get a tetanic contraction. In case of a sufficiently high rate of inter-
ruptions per second the tetanus will be a complete one, during
which no rapid variations of length, thickness or tension of the
muscle can be detected. If the rate of stimulation be lessened, the
tetanus ceases to be a complete one. Synchronous with the stimuli
the muscle shows a series of small twitches superposed on a tetanic
contraction. These can easily be recorded on a rotating drum either
by recording the length, the thickness or the tension of the muscle.
The twitches become slighter by increasing the rate of stimulation.
With a certain rate, which we shall call the critical frequency, they
disappear altogether and we get again a smooth curve, indicating
a complete tetanus.

This critical frequency, with human muscles at least, is fairly
constant and varies only very slightly in different muscles from a
mean of about 18 per second. But is this critical frequency really
a constant one? Do we know of any condition, which might likely
cause a variation?

A complete tetanus is obtained when the frequency of the exci-
tations is such that the intervals between them are equal to the
time required for the muscle, excited by a single instantaneous
stimulus under isometric conditions, to obtain its greatest tension
(BURDON SANDERSON). MAREY and HERMANN among others state that
the time between two stimuli should be a little less than the time
taken by the muscle to reach its greatest tension after excitation
by a single induction-shock. Only changes in the time covered by
the shortening period of the muscle may be able to cause a change
in the critical frequency. It is generally known that temperature
changes and exhaustion alter the form of contraction and that both
act on the ascending part of the curve. With human muscles the
influence of temperature, if any, need not be considered, and in our

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own researches we always took care to experiment only with unfatigued, fresh muscles.

Under these conditions we ought to expect the critical frequency for a complete tetanus to be a constant one, not liable to variation under the influence of pathological changes. If such be not the case we can only conclude that either the form of the complete single-twitch-myogram, or perhaps only its descending part, must be equally significant for the critical frequency as the ascending part of the curve. There is a simple way of solving this question.

A few years ago Dr. DE BOER showed that the tonus-mechanism greatly affects the general form of a single-twitch myogram in a frog's muscle. In a fresh muscle preparation separated from the spinal cord we get only a short myogram, with a rapidly descending part. But in a muscle connected with the nervous system the myogram, and especially its descending part has a much longer duration. The descending line generally shows a secondary elevation — which is often smaller, but may be even larger than the primary apex — called after its discoverer FUNKE's "nose". DE BOER demonstrated that this secondary is a true reflectory tonus-oscillation, which immediately vanishes after cutting the grey rami communicantes from the sympathetic nervous system to the motor plexus. With any variation of the peripheral tonus mechanism the ascending part of the myogram remains unchanged, whereas the descending part is altered in form. We might now ask if the descending part of the myogram does influence the critical frequency for the complete tetanus and we can answer this question by examining the influence of muscle tonus on this critical frequency. A probable connection between the two has been advocated among others by YEO and CASH, who termed tonus the cement connecting the separate muscle twitches so as to form a complete tetanus. BOTAZZI considers tonus as the substratum on which tetanus is built. Also COUSTENSOUX and ZIMMERN state that a direct connection does exist between tonus and the genesis of the complete tetanus.

We have examined a large number of healthy persons with a normal muscletonus as well as clinical cases in which the tonus was either diminished or increased.

The graphic recording of the tetanic muscle contraction caused some difficulty, when as a matter of fact only records of variations in thickness of the muscles could be made. This demanded the greatest care in the construction and use of the recording styluses. Finally by reducing the lever-magnification to 6 times, and by using a lever of only 60 millimeters length and a weight of 11 milligrammes
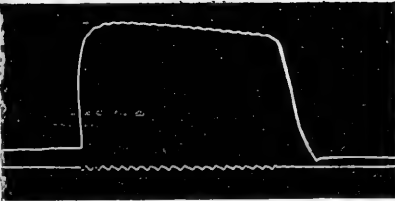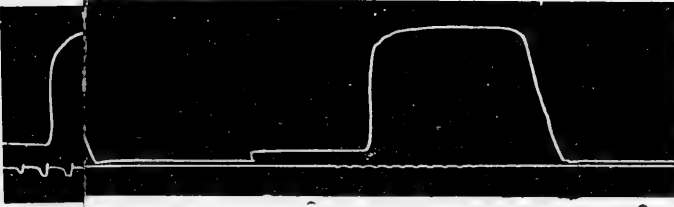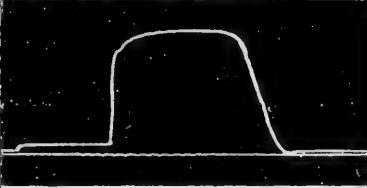
Procee

Fig. 1. Musc gastrocnemius. Commotio cerebri.

Fig. 3. Musc gastrocnemius sinister, indirect. Sclerosis multiplex

Fig. 2. M. Gastrocnemius indirect. Tabes dorsalis

satisfactory results were obtained, comparable with those obtained by means of a Frank-mirror-tambour. Different frequencies were obtained by using 7 different interrupters carefully adjusted to 10, 12, 14, 16, 18, 20 and 22 interruptions per second.

With healthy persons all muscles showed a complete tetanus at a rate of excitation with 20 interruptions per second. With 16 interruptions all the curves showed the characteristic indentations or notches, indicating the rests of the separate muscle twitches. With 18 per second the behaviour of the different muscles showed slight divergencies, some giving a complete tetanus, others still showing the single twitches. As an example of a normal record we give fig. 1, from the gastrocnemius of a healthy woman of 53 years of age. We see 5 tetani obtained successively with 12,14, 16, 18, and 20 stimuli per second. In the curve taken with 18 per second, slight oscillations may still be observed, whereas the last curve may be considered, as a complete tetanus, though the first 2 or 3 stimuli are still visible in the myogram. But this was frequently the case and we considered a tetanus as a complete one when after the 3rd stimulus the oscillations were no longer visible.

If now these curves be compared with those of fig. 2, in which the rate of stimulation was from 12 to 22 per second, we recognize the oscillations even in the last curve, obtained with a frequency of 22 per second. These records are taken from the gastrocnemius of a woman suffering from advanced locomotor ataxia. All the muscles were in an extremely atonic condition.

Lastly we reproduce in fig. 3 the record of faradic tetani of the gastrocnemius at a rate of 12, 16, 18, 20, and 22 stimuli per second. This patient was a man of 45 suffering from sclerosis multiplex cerebrospinalis. All muscles were hypertonic and showed a tendency to contracture. Even with no more than 12 stimuli per second we get a complete tetanus.

The few curves shown are taken somewhat at random from a collection obtained in a large number of healthy persons and patients with either hypertonic or atonic muscles. We always find that in hypertonic muscles the critical frequency is generally 14 or lower, whilst in atonic muscles it is always well over 20.

In the course of our researches we obtained many other interesting records. A few showed a gradual fatigue or exhaustion of the tonus mechanism. Others contained an indication, that under the influence of the contractions an appreciable increase of the tonus occurred. A more detailed description of the experiments and the results will be published elsewhere.

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Anatomy. — *"Is the post-embryonal growth of the nervous system due only to an increase in size or also to an increase in number of the neurones?"* By Erik Agduhr. (Communicated by Prof. J. Boeke).

(Communicated in the meeting of Dec. 28, 1918).

Introduction.

While investigating the effect of training on the post-embryonal development of the nervous system[1]) I was confronted with the following problem. Is there generally an increase in the number of axons during the post-embryonal growth of the nervous system? We are concerned with the roots of the spinal nerves. In the dorsal and ventral roots of the spinal nerves there is, as is shown in more detail below, no *T*- and *Y*-division of the nerve fibres. The problem is thus practically identical with another, viz.: Is there an increase in the number of neurones during the post-embryonal development?

Up to the present time the condition of this question has been such that the possibility referred to has been regarded as almost excluded. This was due to the supposition that the nerve-cells were small bodies so much differentiated that divisions in them could not be imagined. Figures of division of cells in the central nervous system of animals only a few days old have, however, been described, although very eminent investigators, such as Marinesco, Prenant, Valenza, etc. deny that these figures have anything to do with the nerve elements, but consider them to be stroma elements. During recent years the literature points to some extent in the direction of the possibility of a post-embryonal new formation of neurones taking place — although the newly-formed neurones are only considered as replacing those that have been destroyed by degeneration.

The results of the investigation undertaken by me with regard to training (exercising) were of such a nature as to be difficult of explanation in the absence of a real increase in the number of neurones during the post-embryonal growth of the animal. I was

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[1]) So far only a preliminary communication has been published: Der Einfluss der Trainieren auf das morphologische Bild des motorischen Nervensystems Hygiea 1917 (LXXIX).

accordingly compelled to investigate more closely the post-embryonal growth, especially that of the peripheral nervous system.

When these investigations were planned and also during the time when the greater part of the work was being carried out, I was quite unacquainted with the comprehensive American literature connected with this subject, especially the publications of "The Wistar Institute of Anatomy and Biology". It is only a month since I learned about this during a visit to the Central Institute for Brain Research at Amsterdam for purposes of study. For the opportunity of doing so, for the extreme kindness shown to me and for much good advice and valuable criticism I wish to express my most cordial thanks to Dr. ARIËNS KAPPERS and Dr. B. BROUWER. During this journey I also stayed with Prof. J. BOEKE at Leyden and I am deeply indebted to him for his exceedingly cordial reception and very valuable and pertinent criticism. I am also much indebted to my chief, Prof. J. LUNDGREN, for his kindness in revising the English of the manuscript.

The results I obtained in investigating the post-embryonal development of the nervous system confirm in certain points the results obtained by others, especially by "The Wistar Institute of Anatomy and Biology", but on what appear to me to be the most important points my results differ essentially from those of former investigators of this subject. I have attempted to find the causes of this difference and have discovered that they lie in the different methods of investigation that have been used. Previous investigators of this question worked with methods for the staining of medullary sheaths and have determined the number of medullated nerves, whereas I have worked with neurofibril impregnation methods and have determined the number of nerve fibres.

Material and methods.

The majority of the species of animals used in my investigations have, as far as I can find in literature, not been previously subjected to a morphological study of their post-embryonal growth. This was a cause of great trouble to me. It would of course have been more advantageous to use an animal that had been carefully investigated before, when it was a question of explaining something that was essentially new. A very convenient animal of this kind is *Mus norwegicus albinus*, which has been the subject of numbers of detailed investigations concerning its post-embryonal growth at "The

Wistar Institute" and other places. I too shall probably pass on to this animal if I have occasion to continue the present investigations. Although I was unaware of these investigations on *Mus norwegicus albinus*, I have, however, amongst my material a species that is rather closely related to it, namely *Mus rattus* — a male and a female specimen, and their eleven (11) young ones; of the young ones, however, only three (10, 20, and 30 days old respectively) have been investigated up to now. My material consists, in addition, of 58 specimens of *Mus musculus albinus* (of ages ranging from 24 hours to over 2 years). Among these 58 there are several litters — thus, for instance, a male and a female, each over two years old, with several generations of their progeny, 42 altogether. I had also 22 specimens of *Bos taurus* — (half of them two weeks old and the other half over three years — only n. trochlearis and n. oculomotorius were investigated), 5 specimens of *Canis familiaris*, (the two parents and three young ones 6, 17, and 60 days old respectively), a number of specimens of *Felis domestica* (only n. trochlearis and n. occulomotorius have been investigated so far) [1]. Among cold-blooded animals there were 28 toads (*Bufo vulgaris*) of different lengths, ranging from 1,6 to 9,8 cms. from nose to tail — but the number of those that are near the minimum and maximum dimensions is larger than those in between.

The columna vertebralis with its spinal cord and spinal nerves (even including the spinal ganglia of *Bufo*, *Mus musculus* and *Mus rattus*), the central nerve system with the attached sub-dural parts of the spinal and cranial nerves of *Canis* and *Felis* and the sub-dural parts of nn. trochleares and oculumotorii of *Bos* were fixed in a twenty per cent formalin solution. Previous to this convenient spinal ganglia and pieces of the medulla spinalis had been taken out for fixation in FLEMMING's liquid. The material that had been fixed in FLEMMING's liquid was imbedded in paraffin and was partly cut into sections 3—5 μ thick, which were stained with the iron-alum-hematoxylin of HEIDENHAIN and eosin. The material that had been fixed in formalin was impregnated in pieces according to my modifications [2] of BIELSCHOWSKY's method of silver impregnation,

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[1] I shall give a more detailed account of these matters in a subsequent and more extensive publication.

[2] AGDUHR, ERIK, Ueber Stückfärbung mit BIELSCHOWSKY's Silberimprägnations-methode. Einige Modifikationen. Zeitschr. f. wiss. Mikrosk. u. f. mikr. Techn. Bd. 34. 1917.

with the addition that the impregnation in a thirty per cent. AgNO₃ solution was made specially long — over ten days and nights. The impregnated pieces were imbedded in paraffin and were cut into conveniently thick sections, 5—15 μ. A number of spinal ganglia were cut in unbroken series of sections, 10—15 μ in thickness. Cross sections were placed on the sub-dural parts of the spinal nerves, partly close to (centrally of) the spinal ganglia and partly close to the spinal cord. In the preparation, in which the spinal cord and the spinal ganglia had been fixed in situ in the canalis med. spinalis, cross-sections were cut right from the caudal end as far in the direction of the cranium as the sub-dural part of the nerve roots had a caudal course — this was, as a rule, up to the posterior third and the posterior half of the thoracal vertebral column. The rest was cut into sagittal sections, during which the microscope was used to verify that conveniently situated parts of the segmental nerves were present in the sections. These sections were made 5—10 μ thick. In determining the number of nerve fibres in the cross sections I used a LEITZ microscope (tripod G.H.) with a cross-table, an oil-immersion ¹/₁₂ a, and an ocular IV (LEITZ) with the enclosed squared glass plates. It appeared to be necessary to work with such a great magnifying power in determining the number of nerve fibres in order to be able to disintegrate those parts of the preparation in which the nerve fibres were most close, especially in the young animals. Before beginning to count, the square-ocular and the cross-table were adjusted so as to prevent as far as possible unexpected displacements and miscalculations arising from these. Repeated calculations with the same preparations have also shown that the errors in calculation that we are concerned with are small — always less than ten per cent, as a rule not more than five per cent. At first I attempted an approximate method in deciding the number of nerve fibres in the cross-sectioned nerve roots. I counted each nerve fibre in a few hundred squares and found the average number. I then counted the number of squares in a cross-section and multiplied this by the average number. This method appeared, however, to give values that were too uncertain, because nerve fibres of different thicknesses were very unevenly distributed. In order, therefore, to obtain sufficiently exact values, I was thus compelled to count every nerve fibre in the whole cross-section — a method that was certainly troublesome, but necessary in this case, especially with young animals. In counting I always began at the top and at the left, both in the preparation and in the field of the squares, taking care that all the nerve fibres which

were situated on the left and at the top beneath the lines were counted.

A number of spinal ganglia and pieces of the spinal cord (fixed both in FLEMMING and ZENKER liquid and B. impregnated) were arranged in unbroken series for investigation of the figures of cell divisions (sections from 3—5 μ in thickness). Some spinal ganglia with dorsal and ventral roots and a small piece of the spinal cord (all B. impregnated) from animals of various ages were arranged in unbroken series (longitudinal sections of the roots from 5—10 μ in thickness) for investigation as to the occurrence of T- and Y-divisions and figures of growth of the nerve fibres.

The post-embryonal increase in the number of the nerve fibres in the dorsal and ventral roots of the spinal nerves.

With regard to the general growth of whole animals from birth to maturity (or at least during the period of active growth) works have been published on *Gallus domesticus* (MINOT [1]), 1908) *Mus norwegicus albinus* (DONALDSON [2])), *Lepus cuniculus* (MINOT [1]), 1908), *Cavia cobaya* (MINOT [1]), 1891). *Canis familiaris* (ARON, 1911 [1])), *Homo caucas* (ROBERTS, 1878 [1]) and others) and *Homo mongol.* (MISHINA, 1904 [1])), etc. All those who have studied growth have also acknowledged and laid stress on the need for an analysis of the total growth into its components — the organs and their elements the cells. Numerous investigations of the post-embryonal development of the organs and even of the cells have already been published by DONALDSON, HATAI, NAOKI, and others. On the other hand, as far as I could find from the literature, no investigation of a post-embryonal growth of the number of axons in the nervous system seems so far to have been published. It is certainly true that there are numerous investigations on the number of nerve fibres in the dorsal and ventral roots of the spinal nerves and in a number of cranial nerves both in full-grown animals and in animals of different ages (especially *M. norwegicus albinus*), by DUNN, HARDESTY, HATAI and others, and in *Homo* by STILLING, INGBERT and others, but they have all been carried out with the help of staining methods for medullary sheaths and so cannot afford

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[1]) Quoted from DONALDSON, H. H. An anatomical analysis of growth. Trans. of the 5th. International Congress of Hygiene Demography held at Washington D. C. Sept. 23—28. 1912.

[2]) DONALDSON, H. H., WATSON J. B. and DUNN, E. H. 1906. A comparison of the white rat with man in respect to the growth of the entire body. Boas Memorial Volume, New York.

any information about anything but the number of the medullated nerve fibres under different circumstances. As far as the post-embryonal growth -in the number of axons is concerned, these investigations, which in themselves are in many cases very fine pieces of work, afford no information, but with this method one can, of course, only obtain a knowledge of the number of medullated axons, and the total result is that they indicate a gradual process of myelinisation, which is even stated by DONALDSON[1]): "The increase in the number of myelinated fibres in the spinal root with advancing age is due mainly to progressive myelination. Both roots at maturity still contain functional fibres without myelin sheaths (RANSON '06)."

During the progress of the work of counting the number of nerve fibres in the roots of the spinal nerves in the animals I investigated, it soon appeared that it was impossible to get reliable numbers as to the conditions of the nerve fibres in specimens of different ages by counting those in the roots of a single or a small number of spinal nerves. For fairly great displacements and individual variations occur, and these prevent the values from being as good as might be desired, if only a small number of nerves are taken into consideration. On account of this and also in order to obtain an insight into the distribution of the axons in the different regions I have, in most animals, counted each spinal nerve on the same side and in certain specimens on both sides. As I intend to give a more complete and detailed account of these matters in a future work, 1 merely include here some totals from a part of the calculations in question.

By calculating the number of nerve fibres in the same section of the root and by using the method of least squares for the values, it has been shown that the percentage of error in the dorsal roots of very young animals (from four to ten days old) has not exceeded $\pm$ 10, and that for other places it is, as a rule, about $\pm$ 2. (In the dorsal roots of the spinal nerves the nerve fibres are situated very close together in young specimens, so that one has to work with thin (5 μ) sections and strong light in order to obtain exact results). The totals of the dorsal and ventral roots of the spinal nerves given in the tables below are thus to be considered as exact within the limits of the percentages mentioned. That there is thus a post-embryonal increase in the number of nerve fibres in the dorsal and ventral roots is shown with all the clearness that could be desired

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[1]) DONALDSON, H. H. The rat, reference tables and data for the albino rat and the Norway rat, 1915, Philadelphia.

1. Table showing the total numbers of axons in the dorsal and ventral roots of animals of various ages in the same species and of different species.

Species.	Age in days or length in cms.	Total number of axons in all the roots of the spinal nerves.		Relation between the numbers in the dorsal and ventral roots.	Average total.		Percentage of increase.		Remarks.
		ventral roots.	Dorsal roots.		V. r	D. r.	V. r.	D. r.	
Bufo vulgaris.	1.6	3603	4368	1.2 : 1					
,, ,,	1.7	3380	4580	1.36 : 1					
,, ,,	1.7	2947	4156	1.4 : 1					
,, ,,	1.7	3242	4312	1.3 : 1					
,, ,,	1.8	2937	4025	1.3 1	3281	4357			
,, ,,	1.8	3891	4399	1.1 : 1					The average
,, ,,	1.8	3661	4367	1.2 : 1					numbers for
,, ,,	1.9	3130	4650	1.5 : 1					the most dif-
,, ,,	2	2742							ferent sizes and ages of animals are
	1.77 ← average →			1.3 : 1			78	93.8	not reliable, because the increase in
,, ,,	3	4325	6129	1.4 : 1					the axons that is shown
,, ,,	4.5	5065	6614	1.35 : 1					in the table
,, ,,	5.8	5209	6647	1.27 : 1					does not pro-
,, ,,	6.8	5284	7824	1.48 : 1					ceed at an equal pace
,, ,,	7.9	5986	7783	1.3 : 1	5854	8276			during the whole period
,, ,,	9.4	6293	9222	1.46 : 1					of growth.
	8,03 ← average →			1.41 : 1					
Mus rattus ♂	about 700	53260	94109	1.76 : 1	53260	94109			
,, ,, ♀	,, 350	38906	78466	2 : 1			116.9	79.3	
,, ,, ♂	10	24554	52469	2.13 : 1	24554	52469			
,, ,, ♂	30	29252	51338	1.75 : 1					
,, ,, ♂	40	30739	57240	1.86 : 1					
	226 ← average →			1.9 : 1					

2. Table showing the total numbers of axons in the dorsal and ventral roots of animals of various ages in the same species and of different species.

Species.	Age in days or length in cms.	Total number of axons in all the roots of the spinal nerves.		Relation between the numbers in the dorsal and ventral roots.	Average total.		Percentage of increase		Remarks.
		ventral roots.	Dorsal roots.		V. r.	D. r.	V. r.	D. r.	
Mus musc. var. *albus.* ♂	Days 550	23075	48880	2.11 : 1	23067	48639			
„ „ ♀	550	23060	48399	2.09 : 1					
„ „ ♂	189	19588	38122	1.94 : 1					
„ „ ♀	189	18586	37116	1.99 : 1					
„ „ ♂	151	16523	35097	2.12 : 1					
„ „ ♂	77	16215	33888	2.09 : 1			80	105	
„ „ ♂	49	15414	27279	1.76 : 1					
„ „ ♂	25	14236	26136	1.8 : 1					
„ „ ♂	10	12825	23874	1.86 : 1					
„ „ ♂	10	12762	24190	1.89 : 1					
„ „	4	12431	23824	1.9 : 1	12814	23715			
„ „	4	12497	23311	1.86 : 1					
„ „	4	12936	23432	1.81 : 1					
„ „	4	13432	23663	1.7 : 1					
	129 Days	15970	31229	1.92 : 1	← Average				
Canis fam. ♀	about 2190	183188	393489	2.14 : 1	183188	393489			
„ „ ♂	„ 1277	139808	278879	1.99 : 1			72.7	73.9	
„ „ ♀	6	106072	226264	2.13 : 1	106072	226264			
„ „ ♀	17	134867	245089	1.81 : 1					
„ „ ♀	60	124401	237839	1.91 : 1					
	710	137667	276312	2 : 1					

by the above table, which also illustrates to some extent the magnitude of the increase. The increase in the number of axons is proportionately greater during the first part of the period of growth than during the latter part, which is probably not completed in any of the group of animals included in the table. It is interesting to

compare briefly the results arrived at by some of the previous investigators of this subject. The latter have, however, worked with myelins sheath staining methods and have determined the number of medullated nerve fibres in different states.

DUNN [1]) "A considerable increase in the number of medullated nerve fibres occurs during the early life of the albino rat". DUNN investigated the ventral root of C II in *Mus norweg. albinus.* The same thing is true, according to HATAI [2]) of the "albino rat" with regard to the ventral roots of C VI, Th IV and L II, and, according to BOUGHTON [3]), with regard to n. occulomotorius in the same animal. BOUGHTON's investigations (06) about cognate problems in the cat and WILLEMS's [4]) in the rabbit point to the same conclusion.

DUNN states: "RANSON's records then are comparable with those presented now, and together they show that in regard to the second spinal nerve of the albino rat the number of medullated nerve fibres in both the dorsal and ventral nerve roots increases during the life of the individual, but that the greatest increase occurs before the sexual maturity or so-called puberty of the animal," and so on. It is thus shown that what is true in this respect for all the axons — as shown by the results of the calculations given in the above table — is also true for only the medullated nerve fibres. The percentage of increase obtained by using myelin sheath staining methods on the material in question is considerably larger than that arrived at by impregnation of the axons. This is due to the fact that the young animal has relatively considerably more axons free from medullary sheaths than the older one. This increase in the number of nerve fibres is decidedly larger in the dorsal than in the ventral roots, a fact which is seen most clearly when the comparison is based on the conditions in a rather large number of animals. This is not so striking in *Canis*, and *Mus rattus* shows an entirely reversed state of affairs. These apparent exceptions are, however, probably due to

[1]) DUNN, ELISABETH HOPKINS. The influence of age, sex, weight and relationship upon the number of medullated nerve fibres and on the size of the largest fibres in the ventral root of the second cervical nerve of the albino rat. The Journ. Comp. Neur. Vol. 22. N⁰. 2. 1912.

[2]) HATAI, SHINKISKI. On the increase in the number of medullated nerve fibres in the ventral roots of the spinal nerves of the growing white rat. J. Comp. Neur. Vol. 13, 1903.

[3]) BOUGHTON, THOMAS HARRIS. The increase in the number and size of the medullated fibres in the occulomotor nerve of the white rat and of the cat at different ages. J. Comp. Neur. Vol. 16. 1906.

[4]) WILLEMS, EDOUARD. Localisation motrice et kinesthesique. Les noyaux masticateur et mesencephalique du trijumeau chez le lapin. Le Neuraxe t. 12, 1911.

the fact that the numbers for these animals were based on speci-
mens on a few investigations. The difference between the number
of nerve fibres in the dorsal and ventral roots is comparatively
greater in old than in young animals of the same species. I shall
leave a more detailed discussion of the values obtained for a future
and more complete account of the questions that are connected with
this problem and shall pass on instead to an attempt to answer the
following question :

*How does a post-embryonal increase in the number of axons in the
dorsal and ventral roots of the spinal nerves arise?*

This question forces itself upon our attention when we find that
the number of nerve fibres in the dorsal and ventral roots of the
spinal nerves increases considerably with the growth of the animal.
There may, however, be different opinions as to the manner in which
this increase takes place, and this question certainly needs to be
subjected to a comprehensive investigation. There are really two
possibilities to be taken into consideration. *The increase must depend
either on a T- or Y-formed division of nerve fibres, or on an outgrowth
from the centre, from nerve cells* (neuroblasts) *that have been newly
formed or are lying in reserve.* There is, of course, a third possibility
which is, however, not very probable, namely, *that one nerve-cell
has discharged two axons in the same direction.*

*Does a division of the nerve fibres exist in the roots of the spinal
nerves?*

Most obvious is of course the supposition that we have here a
cleavage (*T*- or *Y*-division) of the nerve fibres on the lines of the
process, of which such fine examples may be seen in the peripheral
part of the nerves and also in the central nerve system. A cleavage
of this kind may be exceedingly frequent; thus, at Prof. BOEKE's in
Leyden I saw a preparation which showed, among other things,
a nerve fibre that was divided at one place into six branches.
STEFANELLI [1]) describes and reproduces a preparation from the tongue
of the chameleon, in which a single nerve fibre was divided into
branches terminating in no less than thirty-five motory plates. During
nerve regeneration after a section one may also see abundant
examples of such division. See, for instance, the figures in CAJAL [2])

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[1]) STEFANELLI, A. La piastra motrice secondo le vecchie e le nuove vedute.
Annali di Neurologia Fasc. IV 1912. Quoted by BOEKE L. c. 3.

[2]) CAJAL, RAMON Y. Studien über Nervenregeneration (J. A. Barth, Leipzig) 1908.

and BOEKE[1]). NAGEOTTE[2]) reproduces and describes spinal nerve-cells, in which a collateral leaves the axon quite close to the nerve-cell. This collateral terminates in a club-like swelling, which is situated inside the capsule of the same nerve-cell. N. is of opinion that these collaterals are due to regenerative activity in the cell, with which CAJAL[3]) also agrees. BIELSCHOWSKY[4]) interprets these formations in another way; he includes them among the fenestrate cells and thinks that these processes have nothing to do with regeneration. RANSON[5]) has tried to discover an explanation of this phenomenon by means of experiments. The results given by these experiments have, without exception, indicated that these processes with club-like formations are not a product of regenerative activity in the cell. I have however, been unable to find in the literature any indication of the fact that T- and Y-divisions occur in the dorsal and ventral roots of the spinal nerves. As a working hypothesis for my continued investigations I took the possibility (which is, in itself, not at all probable) that the above-mentioned, or similar, processes with club-like formations might develop into axons and, in addition, the possibility that T- and Y-divisions might occur in the intra- and extra-medullar course of the ventral roots as well as in the dorsal roots, which would explain the post-embryonal increase in the axons there which is under discussion.

Silver impregnated dorsal and ventral roots of lumbal and sacral nerves in connection with their spinal ganglia, and a small piece of half the spinal cord on the same side from animals of different ages within the same species, were set up in unbroken series (10μ thick). These series were well suited for studies of the figures of the growth that might possibly occur, and for investigations made with a view to answering the third possibility that had been advanced, namely whether one nerve cell, the axons of which form the spinal nerves, sends off more than one axon in the same direction. In investigating the preparation a cross-table was used and the microscope was

[1]) BOEKE, J. Studien zur Nervenregeneration II Verhandel. d. K. Akad. v. Wet. te Amsterdam. Deel XIX. N⁰. 5. 1917.

[2]) NAGEOTTE, J. Recherches experimentales sur la morphologie des cellules et des fibres des ganglions rachidiens Rev. Neurol. Paris. Vol. 15, p. 357.

[3]) CAJAL S. RAMON Y. Die Struktur der sensiblen Ganglien des Menschen und der Tiere. Anat. Heft. Zweite Abt. Bd. 16. 1907.

[4]) BIELSCHOWSKY, M. Ueber den Bau der Spinalganglien unter normalen und pathologischen Verhältnissen. J. Psych u. Neur. B. 11, 1908. Leipzig.

[5]) RANSON, S. WALTER. The Structure of the Spinal Ganglia and of the Spinal Nerves. J. Comp. Neur. Vol. 22. 1912.

provided with an oil immersion ($^{1}/_{12}$ a) and ocular four. The preparations were investigated in the most careful way step by step, but not a single example of a division of the nerve fibres could be discovered, either in the roots or in the continuation of the nerve fibres in the ventral horn through the spinal cord up to their root cells. I observed a few cases of spinal ganglion-cells which had the claviform processes mentioned above. These claviform formations were, however, always within the capsules. In no case, however, was I able to discover anything that could be interpreted as a division within the spinal ganglion of either the central axon or that which passes peripherally. I tried to test the negative results obtained from this investigation in another way, in order to obtain if possible a positive result. I made cross-sections of the silver impregnated material through the corresponding nerve roots on the
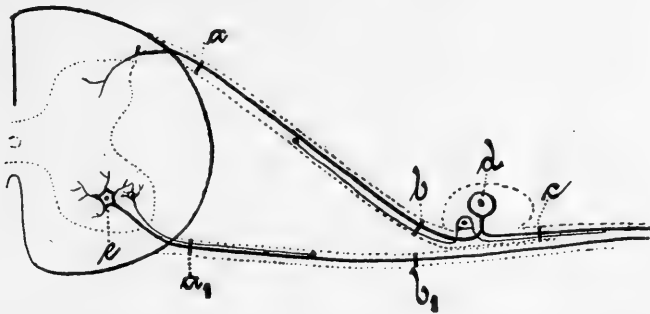
Fig. 1. Schematic representation of the neural growth in the dorsal and ventral roots of the spinal nerves. (*a*) Cross section at the place with the smaller and (*b*) cross section at the place with the larger number of nerve fibres in the dorsal root. (*a*$_1$) Cross section at the place with the larger and (*b*$_1$) cross section at the place with the smaller number of nerve fibres in the ventral root at a spinal nerve from a young animal. (*c*) Cross section peripherally of the spinal ganglion. (*d*) Spinal ganglion cell. (*e*) Ventral root cell.

other side, some close to the spinal cord (*a* and *a*$_1$; fig. 1) and others close to, but centrally of, the spinal ganglion (*b* and *b*$_1$; fig. 1). As the nerve roots that I investigated belonged to the lumbal and sacral nerves, which take part in forming the quada equina, the distance between the two cross sections was fairly great. The nerve fibres in the sectioned preparation were counted. There are three possibilities for the totals that we might expect to obtain for the numbers of nerve fibres. If we take *a*; *a*$_1$; *b* and *b*$_1$ fig. 1 to denote the number of nerve fibres, then $a = b$ or else $a > b$ or finally $a < b$. If $a = b$ then one could scarcely expect any appearance of axon-division or any figures of growth in the piece *ab*; if, on the

other hand, $a > b$; then one ought to succeed in finding figures of division of the nerve fibres in ab; if, finally, $a < b$, then, of course, one ought to be successful in finding figures of growth in ab. For the ventral root the corresponding line of argument is, of course, as follows: if $a_1 = b_1$, then there are probably neither figures of division nor growth in the piece a_1b_1; if $a_1 > b_1$, there are probably figures of growth in a_1b_1; if $a_1 < b_1$, there are probably figures of division in a_1b_1.

In not a single case did the calculations that were carried out give values for a that were greater than those of b, nor values for b_1 greater than those of a_1. The two values for each root in older animals were — apart from the possibility of error (about 2%) — equally large. In young animals, on the other hand, as a rule $a < b$ and $a_1 > b_1$. As examples we may give the values for S. 1 (left side) in a puppy sixty days old: $a = 9209$, $b = 11487$; $a_1 = 3335$, $b_1 = 2623$.

If we correct these numbers according to the percentage of error in the calculation, we then obtain: $a = 9209 + 2\% = 9393$, $b = 11487 - 2\% = 11251$; $a_1 = 3335 - 2\% = 3268$, $b_1 = 2623 + + 2\% = 2675$.

These figures are very clear evidence against the occurrence of any figures of division in the pieces ab and a_1b_1 respectively in the animals in question. On the other hand they indicate, of course, the existence of a not inconsiderable number of figures of new growth of axons. As far as I can see, I have found a small number of certain figures of new growth — there are undoubtedly more of these. These formations vary, of course, very greatly in their form. Such great differences in the number of nerve fibres in a and b and a_1 and b_1 are, however, not always found even in young animals; the differences are, as a rule, considerably less.

I could not discover any possible method of verifying more effectively the above-mentioned absence of any T- and Y-division in the spinal cord and the spinal ganglia of the nerve fibres that pass into the roots, and have consequently to be content with the fact that in the above-mentioned preparation no figures of division could be detected in these parts. It might perhaps be said that the number of cells in the ventral horns and in the spinal ganglia compared with the number of axons in the ventral and dorsal roots respectively might afford a means of verification. This is not the case, however, as the number of the ganglion-cells in both the ventral horn and in the spinal ganglion is always considerably greater than the number of axons. (This is discussed in greater detail below.)

As this attempt to explain the increase actually existing in the number of nerve fibres in the dorsal and ventral roots of the spinal nerves as a result of a division of the axons was unsuccessful, I had to proceed to investigate other possibilities. The following possibility has now to be closely considered.

Is it possible that a nerve-cell may send off more than one axon in the same direction?

In order to be able to answer this question, I have carried out investigations in two directions. I first investigated carefully the preparations left over from the preceding series in which, of course, whole spinal ganglia and parts of the ventral horn were set up in unbroken series, and secondly I counted all the cells in a ventral horn of a 10 days' old and of a 360 days' old *Nus musculus var. albus* — between the exits for two spinal nerves from corresponding segments — and also all the cells in a spinal ganglion similarly situated in the two animals. The values obtained for the numbers of cells have been compared with the number of axons in the corresponding ventral and dorsal roots. One cannot, of course, expect to obtain in these two ways an answer to the aforesaid question that would be a priori absolutely certain, but it seems to me that they take us as far as we can generally go with morphological methods of investigation. A careful investigation (of the above-mentioned unbroken series) of the nerve-cells in the ventral horns and in the spinal ganglion did not produce a single figure to support the supposition of more than one axon being sent off in the same direction from the nerve-cell. It is certainly true that in the spinal ganglion there were nerve-cells which have processes beside the axon, but in no single case could these be followed up to a T-division. Spinal ganglion-cells of this sort are described by RANSON [1]) and others. I am of the opinion that this part of the investigation produced a negative result.

With regard to the calculations as to the number of cells, they showed that the number in the older specimen was certainly greater than in the younger one, but the difference is not so large compared with the difference in the number of axons in the same specimens. The number of axons seems thus to increase in a relatively higher degree than the number of ganglion-cells during the post-embryonal period. This fact seems, of course, to allow the possibility that the same nerve-cell might send more than one axon into, for instance, the dorsal and ventral roots. There is, however, another and more

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[1]) L. c.

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probable, even a certain, way of explaining this phenomenon, namely that in both the spinal ganglia and the central nerve system there are young cells which have not hitherto sent out any axons, and which have the power of dividing. (This point is discussed more completely below). Such cells are considerably more numerous in young specimens than in older ones. I am thus of the opinion that this part of the investigation has not given any support either to an assumption of the possible occurrence of nerve-cells that send two axons into the dorsal or ventral root. Nor have I found in the literature any statement that points to this conclusion. It thus still remains to investigate other possibilities.

Do axons grow either from newly formed or from older nerve-cells lying in reserve.

This part of the investigation, which I tried to avoid as long as possible, in the hope of finding other explanations of the post-embryonal increase in the axons, has, however, gradually become the most central — the main part, on which the entire result is based. Observations made here and there in the preceding parts of the investigation indicated clearly that the solution to the problem was to be sought in this direction. Such a solution, however, does not quite agree with the hitherto prevailing view as to the development of the nerve system and the character of the neurones. There is, however, as we shall see, an abundance of facts to support this solution. I shall begin with an examination of the

Spinal ganglion.

HEIDENHAIN, M.[1]) writes: "Es würde gewiss für die Physiologie von grosser Bedeutung sein wenn wir behaupten könnten, dass wir mit der Anatomie der cerebrospinalen Ganglien im reinen sind. Dies ist jedoch nicht der Fall. Erstlich ist der Ursprung der erwähnten afferenten sympathischen Fasern leider nicht näher bekannt und zweitens befindet sich nach der Zählung von GAULE und LEWIS, ebenso von BÜHLER, in den Ganglien eine ausserordentliche Ueber-zahl von Zellen deren Fortsätze wir noch nicht kennen".

Among the many investigations concerned, among other things, with the making of comparisons between the number of *medullated* nerve fibres in the dorsal root and the number of cells in the spinal ganglion belonging to the root, the following may be cited:

[1]) HEIDENHAIN, M. Plasma und Zelle. Jena 1911.

TABLE *a*.

Author.	Animal.	Nerve.	Number of nerve cells.	Number of modullated fibres in the dorsal root.
GAULE and LEWIN [1])	Rabbit	Cocc. I	20361	3173
HATAI [2]) (02) .	White rat	C. VI	12200	4227
HATAI [2]) (02)	„ „	L. II	9442	1644
RANSON [4]) (08)	„ „	C. II	7721	2472

From this table we see that the number of nerve-cells is many times greater than the number of medullated axons in the dorsal root belonging to them. HATAI [3]) has investigated the relation between the large and the small cells in the ganglion spinale and has found that in the white rat the small ones are about 60 per cent of the total number. In the case of C II in the cat, WARRINGTON and GRIFFITH [5]) have found that the small cells in the ganglion compose about 70 per cent of the total number. HATAI has investigated the number of cells, both large and small, in the spinal ganglion and the number of medullated nerve fibres in the dorsal roots of C VI, Th IV and L II in animals of different ages of *Mus norvegicus albinus*. A résumé of the values obtained by him is given in the following table *b*°. (See table *b* following page).

With regard to the views of different writers on this subject as to the number of nerve fibres in the dorsal root and the number of cells in the spinal ganglion, all are agreed that the number of cells is considerably greater than the number of medullated axons. Those mentioned above have also investigated this relation only according to the medullary sheath stains. RANSON, who has *Cajal*-impregnated a spinal ganglion and the dorsal root appertaining to this from a dog, has shown the existence of non-medullated fibres in the dorsal root, which he supposes to issue from the small cells in the

[1]) GAULE und LEWIN: Ueber die Zahlen der Nervenfasern und Ganglienzellen des Kaninchens. Centralbl. f. Physiol. Heft. 15 u. 16, 1896.

[2]) HATAI S. Number and size of the spinal ganglion cells and dorsal root-fibres in the white rat at different ages. J. Comp. Neur. Vol. 12.

[3]) HATAI, S. Preliminary note on the presence of a new group of neurones in the dorsal roots of the spinal nerves of the white rat. Biol. Bull. Vol. 3.

[4]) RANSON, S. W. Retrograde degeneration in the spinal nerves. J. Comp. Neur. and Psychol., Vol. 16. Quoted by DONALDSON l. c. (1915).

[5]) WARRINGTON, W. B. and GRIFFITH, F. On the cells of the spinal ganglia and of the relationship of their histological structure to the axonal distribution. Brain. Vol. 28. Quoted by Ranson. 1912. l. c.

spinal ganglion. R. writes: "It is to these non-medullated fibres, the axons of the small spinal ganglion cells, that we are to look

TABLE b.

Weight of the body		Total num-ber of cells.	Large cells.	Small cells.	Relation between large and small cells.	Medul-lated axons.	Relation be-tween the medullated axons and the cells.	Relation be-tween medul-lated axons and the large cells.
C. VI	10,3	10996	2526	8470	1 : 3,4	1998	1 : 5,5	1 : 1,2
	24.5	9793	2395	7398	1 : 3	2569	1 : 4	1 : 0,92
	68,5	11772	3546	8226	1 : 2,3	3683	1 : 3,2	1 : 0,97
	167	12200	5080	7120	1 : 1,4	4227	1 : 2,7	1 : 1,1
Th IV	10,3	7142	1557	5585	1 : 3,5	607	1 : 1,1	1 : 2,5
	24,5	7068	1824	5244	1 : 2,9	863	1 : 8,2	1 : 2,1
	68,5	7611	2370	5241	1 : 2,2	1420	1 : 5,3	1 : 1,6
	167	7406	2902	4404	1 : 1,5	1522	1 : 4,3	1 : 1,2
L II	10,3	8315	1902	6413	1 : 3,4	723	1 : 11,5	1 : 2,6
	24,5	8200	2044	6156	1 : 3	911	1 : 9	1 : 2,6
	68,5	9514	2934	6580	1 : 2,2	1317	1 : 7,1	1 : 2,2
	167	9442	3677	5765	1 : 1,5	1644	1 : 5,7	1 : 2,2

for the explanation of the discrepancy between the number of spinal ganglion cells and medulated afferent fibres. If a count were made the number would probably closely approximate to that of the spinal ganglion cells." Thus RANSON thinks that in this way he has solved the problem quoted from HEIDENHAIN above. If, however, we examine the figure 15 that R. includes in his work, we see that all the black spots in this drawing cannot be axons, but that, if all points exist in the preparation, most of them are probably precipitates of silver. On the other hand a large number of these black dots, which one can with good reason assume to be axons, show traces of a medullary sheath. It is, however, difficult to decide such a matter when one has not seen the preparation in question, but only what is perhaps a skeleton drawing. My own investigations on this point show, however, that R. has gone too far when he writes "If a count of the afferent fibres were made, the number would probably closely approximate to that of the spinal ganglion cells."

It is true that in counting the nerve fibres on the silver impreg

nated dorsal roots I have seen some non-medullated fibres, but they have never occurred in my preparations in as great numbers as R. seems to have seen them. A large number of these finer fibres have, as one finds on closer investigation, a medullary sheath, although rather a thin one. This fact has caused me to undertake a closer and renewed examination of the question of the relation between the total number of nerve fibres in the dorsal root and the total number of ganglion cells in the spinal ganglion belonging to this.

From the right side of a 3,5 years' old dog the spinal ganglia with their dorsal roots from Th VI, L IV and L VII were taken. After fixation and silver-impregnation (according to my modifications of the B.-method) the spinal ganglia were put in unbroken series of sections, 15 μ thick, and the cross-sections at b and c fig. 1 were made 10 μ thick.

The results obtained were as follows:

Th. VI. Total number of ganglion-cells $= 8422$
,, ,, ,, nerve-fibres at $b = 6198$
,, ,, ,, ,, ,, $c = 6297$
L IV. Total number of ganglion cells $= 12181$
,, ,, ,, nerve-fibres at $b = 9003$
,. ., ,, ,, ,, $c = 9311$
L VII. Total number of ganglion cells $= 29621$
,, ,, ,, nerve-fibres at $b = 23627$
,, ,, ,, ,, ,, $c = 23987$

These figures show that, although each nerve fibre in the dorsal root is counted, one does not reach the total number of the spinal ganglion cells. This is also the case if one counts the nerve fibres situated immediately peripherally from the spinal ganglion. The slightly larger values of the latter nerve fibres are all within the limit error in calculation (± 2 per cent). Thus one cannot conclude from these figures that the nerve fibres which issue out of the spinal ganglion into the nerve are more numerous than those which form the dorsal root. It was noticeable that the medullary sheaths were more powerfully developed at c than at b fig. 1. On the strength of the results of my own investigations I wish to state that RANSON goes too far, and that the other writers who have worked with the method of medullary sheaths do not go far enough in their conclusions with regard to the relation between the number of ganglion cells and the number of nerve fibres in the dorsal root. Here, as in so many other cases, the motto "in medio veritas" applies. Thus, in spite of RANSON, we must take into account the fact that the

number of ganglion cells exceeds the number of axons and that this excess must have some significance.

From the silver-impregnated series we obtain an indication of the purpose of this excess in the number of cells. We find that, however intensively the spinal ganglia are impregnated — especially in young animals — there are, all the same, a number of cells that cannot be impregnated, in spite of the fact that the adjacent cells show the most splendid neuro-fibril structures. It is, however, not always the smallest cells that cannot be impregnated, but a number of average-sized ones as well, while others of the smallest and the average-sized ones show exceedingly fine impregnation. The question why this or that cell is not impregnated naturally arises. This is by no means the first time that attention has been drawn to the different powers for intensive impregnation shown by the spinal ganglion-cells. Even in his work on "Zell substanz, Kern und Zellteilung" and in the presentation volume to HENLE, FLEMMING points out that cells are stained to different degrees of intensity by the same colouring matter, and is of the opinion that this is due to greater or less density in the colourable fibres of which the protoplasm is constituted. FLESCH, GITISS, KOTLAREVSKY, KONEFF and MÜLLER [1]) and others have dealt with this subject more or less thoroughly. FLESCH and his pupils, and MÜLLER among others, have studied the capacity for staining possessed by the ganglion cells. KONEFF states that the different capacities for staining are not connected with certain species or cells with special morphological characteristics. The cells are large and small, of different shapes, and some of them are distinguished by their chromatic nucleus. For the two kinds of cells — the strongly and the weakly stained — this author suggests the names of chromophila and chromophoba ganglion cells. The author supposes that some of these different cells are in different functional stages and others are developed to different degrees. MÜLLER distinguishes a type of spinal ganglion cells that have, among other characteristics, strongly eosinophile protoplasm and nuclei rich in chromatin; these cells he takes to be developing forms. It is thus not only in silver impregnation, but also with ordinary nuclei and protoplasmic impregnations that this different intensity in the impregnation appears. With regard to these conditions in the BIELSCHOWSKY-preparation, they indicate to some extent, as has been mentioned, cells with elective neurofibril impregnations and to some extent cells in which no neurofibril

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[1]) MÜLLER, ERIK: Studien über die Spinalganglien. Biolog. förening. förhandl. Bd. 1. 1888—89. Stockholm. Other statements in the literature that touch on this subject are referred to here.

structures appear, but where the protoplasm has a marble appearance. The cells with the evident neurofibril structure may be of the most varying sizes and may also occur in different stages of development; this is shown, among other ways, by the fact that in mammals of post-foetal ages a few bi-polar cells are found in this group, besides the ordinary unipolar cells, (see fig. 12). The cells that are without any neurofibril structure, or have merely traces of this, are similarly of very different sizes, and on several of them I have found formations which could hardly be interpreted otherwise than by assuming that the cell is dividing amitotically. On the other hand I have not in a single case been able to observe any indications of amitotic division in a cell of the former type, in which the neuro-fibril structure was evident. The apolar cells also belong to this category.

In a number of preparations from the spinal ganglia of young animals (dogs) I have found colonies of nerve-cells situated within the same capsule. The number of cells in these colonies varied considerably. Fig. 4 shows one of these colonies with seven cells, in which at a few places protoplasmic bridges (bridging fibrils) go from one cell to the other; there are no processes, and the cells show a pale shade of colour; there is no neuro-fibril impregnation. The references in literature to this condition and a more detailed description of it will be given below. Traces of this difference in neuro-fibril impregnation which is found in the spinal ganglia are also seen in the central nerve system, although it is not so striking there.

These facts have led me to set up the following working hypothesis: The affinity of the neuro-fibrils in the nerve-cells to the silver salts (reducing power) seems to vary from being more or less powerful to total disappearance during certain metabolic or functional stages. The majority of the pale cells seem thus to belong to such an early stage of development that no neuro-fibrils have yet been fully developed in them.

We have now reached the heart of the problem of division, viz. the increase of the ganglion cells in the spinal ganglion. With regard to this problem HATAI [1] writes as follows: "We can only say at present concerning the division problem that the nerve cells in vertebrates, as well as in invertebrates, have the centrosome and the sphare, which are regarded as the dynamic centres of the mitotic divisions, and, further, that this centrosome is able to take the first

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[1] HATAI, S. On the Presence of the Centrosome in Certain Nerve Cells of the White Rat J. Comp. Neur. Vol. XI. N⁰. 1. 1901.

steps of division under certain forms of stimulation, as has been observed by some investigators; but in the normal state the centrosome in an adult cell presents slight morphological differences from that of the embryonic cell, which we interpret as the beginning of degeneration". HATAI comes finally to the conclusion that the only way to find out whether there is generally a division of ganglion cells in the spinal ganglion is to count the number of ganglion cells in corresponding ganglia in animals of different ages. HATAI counted the ganglion cells in C VII, Th IV and L II in four specimens of *Mus norwegicus albinus* weighing 10,3, 24,5, 68,5 and 167 grammes respectively. I have given a synopsis of the results of his calculations in Table *b* above. At the outset I wish to make this criticism on his calculations, namely, that he has contented himself with counting the number of ganglion cells in only one spinal nerve in each of the cervical, thoracal and lumbal regions. Great variation may exist in these, as I have had abundant opportunities of observing during my counting of axons. These variations may be so great that, in a species in which the total increase of the number of nerve fibres in the dorsal roots during post-embryonal growth is, let us say, 100 per cent., certain nerves in the few days' old individual may, in spite of this, contain more nerve fibres than the corresponding nerves in the full-grown animal.[1]) My continued investigations have also shown that a similar variation may be found in the number of ganglion cells in the spinal ganglion. In this case one has to investigate a rather large number of spinal ganglia in order to obtain reliable information by the method used by HATAI. On account of the values obtained by counting (Table *b*) H. concludes that "the total number of the spinal ganglion cells remains approximately constant between 10,3 and 167 grams, though individual variations in the numbers of the cells in corresponding ganglia exist. It can therefore be stated that this number does not increase or decrease with age." We must, however, note that the number of ganglion cells was throughout larger in the older specimens (Table *b*), although the excess in the numbers was not so great. HATAI puts these larger numbers of cells in the older individual within the limits of the variations. It seems as if he cannot admit the possibility that a division of cells in a spinal ganglion might occur. HATAI reveals this especially in his criticism of BÜHLER's[2]) observations. BÜHLER writes:

"Es kommt wie ich mich bei Frosch und Kröte und auch beim

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[1]) Further details about this will be given in the more complete account.

[2]) BÜHLER, A. Untersuchungen über den Bau der Nervenzellen. Verh. d. Phys. med. Ges Würzburg. N. T. Bd 39, 1898 Cit. nach HATAI (1902).

Kaninchen überzeugen konnte, physiologischer Weise zum Untergang speziell der grossen Spinalganglienzellen. Die Degeneration verläuft in verschiedenen Formen und allem Anschein nach wenig rapid. Man siet in einem Spinalganglion des Frosches c.a. 20—25 untergehende Zellen, beim Kaninchen relativ noch viel weniger. Die verloren gegangenen Zellen müssen ersetzt werden und dies geschieht wahrscheinlich dadurch, das eine der kleinen durch Wachstum ihre Stelle einnimmt. Da nach dem frühesten Jugendstadium eine Vermehrung von Nervenzellen nicht mehr vorkommt, muss das Spinalganglion, um für die Zeit des Lebens funktionsfähig bleiben zu können, in der Anlage genügendes Ersatzmaterial in Gestalt von Reservenzellen mitbekommen. Genauere Untersuchungen hierüber zu machen, bin ich indessen noch nicht in der Lage gewesen.'' With regard to this HATAI states: "The above interpretation given by BÜHLER concerning the small cells cannot be accepted as far as white rats are concerned, for he regarded the small cells as replacing the degenerated large nerve cells; if this were the case, then the total number of the spinal ganglion cells must be decreased, but the preceding table shows that the total number is approximately constant.''

I have observed in a number of cases in preparations from dogs that a number of the larger nerve-cells in the spinal ganglion show signs of being in process of degeneration, and in my opinion BÜHLER is right in saying that these degenerating cells are replaced by young cells which grow out in their place. HATAI's argument to the contrary: "If this were the case, then the total number of the spinal ganglion cells must decrease" proves nothing at all. It is even fairly certain that the degenerate cells are replaced by young cells, which grow out and, notwithstanding this degeneration, increase the absolute number of ganglion cells during the post-embryonal growth. As a matter of fact, HATAI has unconsciously proved this last point by his calculations (Table b), and his evidence in favour of it would certainly have been very much clearer if he had made use of greater material and had counted the cells in a larger number of corresponding spinal ganglia in the animal investigated.

The calculations I am making (which I have, however, not yet completed) of the number of ganglion cells in the spinal ganglia of animals of different ages in the same litter, seem to show that there really is an increase in the number of ganglion cells during post-embryonal life, although this increase is not nearly so large as the increase in the axons. My preparations have also afforded information as to the way in which this increase is brought about.

(*To be continued*)·

ERRATA in Proceedings Vol. **XX**

p. 1168 line 4 from the bottom: read 0.99165 for 0.99265.
p. 1174 last line: read "about —210°C." for "about 210°".

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Geology. — *"On the Secretion of Phosphates in the stems of Djatikapur [Tectona grandis L.]"*. By Prof. A. Wichmann.

(Communicated in the meeting of November 30, 1918).

The natives of the Indian Archipelago designate the nodular secretions in organisms, no matter whether they are of vegetable or of animal origin as *mestika*[1]). Petrifications are also sometimes included among them. To some of those formations people ascribe a healing power or they are used as talismans, as is the case among other peoples.

Such secretions occurring in the wood tissue of trees — *mestika kaju* — were first revealed by G. E. Rumphius; he, however, adduced only few specimens. He detected them in the stems of *Casuarina* in the gowasa- or kofaso-wood (*Vitex Cofassus* Reinw.) in the sanga-wood (*Tristania obovata* R. Br.) and in the concretions of the *kemuming-batu* (*Murraya?*), which he classified as *dendritis arborea*[2]). It is remarkable, though, that he remained ignorant of the fact — like other old writers — that the Djati-tree[3]) (*Tectona grandis* L.) known to him, sometimes contains secretions, which, as to size and quantity, surpass those of all plants. He, indeed, reports one description, viz. that of the *djati batu*, (stone-djati), but since he considers it to be the best kind and does not mention any petrous concretions, it can hardly be identified with the *djati kapur*. Although it cannot be doubted that the Javanese, who have ever made a frequent use of *Tectona*-wood, were acquainted with *djati-kapur*[4]), the first mention of this variety is found in a report presented by Thomas Hornfield

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[1]) Among the first-mentioned the best known are the *mestika awi* — the *tabaschir* occurring in the knots of bamboo — and the *mestika kalapa* — secretions from calciumcarbonate in cocoanuts. Rumphius also enumerates: *mestika bras, mestika gondu, mestika nangka, mestika pinang* and *mestika pisang*. Among those from animal organisms are noted the *mestika ular* (snakestone) the *mestika babi* (*pedra de porco*) and the *bezoar*.

[2]) "D'Amboinsche Rariteitkamer", Amsterdam, 1705, blz. 323. To my knowledge not one of those formations have been examined. Of them there is consequently no record in the literature.

[3]) Herbarium Amboinense, 3, Amsterdam 1743, blz. 34—36.

[4]) *Kapur* means lime.

to Marshal DAENDELS on May 31, 1808 [1]), referred to by C. L. BLUME in 1859 [2]).

Architectural experts and shipbuilders evinced a greater interest. H. DE BRUYN asserted in 1851 that *djati kapur* is considered to be of the least quality, "on account of the calcareous secretions found in it". [3]) A little more is said by C. G. VON DENTSCH, when he tells us that "the tree is named after the veins of sulphuric acid lime, which are often visible over the whole length of the stem and seem to be owing to the lime particles ascending with the saps" [4]). Two years later F. JUNGHUHN called attention to the fact .that those secretions were restricted to the specimens of *Tectona* growing on lime-marl deposits, such as are found especially in the residences of Rembang and Surabaya [5]). Some geologists disagree as to the nature of these secretions. Whereas VON DENTZSCH takes them to be calcium-sulphate, HERMAN CRÜGER (1857) holds that "*Tectona grandis*" is "nach ihrem durch das Mikroskop bestimmbaren Gehalt an Kiesel eine schwache Kieselpflanze", but he omits telling us how he could establish the presence of siliceous particles. He also fancied he had observed "dass die Zellwände von kohlensauren Erden eingenommen und sich zwischen grossen Kieselkörpern ohne bestimmbare Formen befinden". [6]). Subsequent investigators have not detected this either and

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[1]) For aught I know H. W. DAENDELS was the first to report *djati kapur*. In Art. 39 of his "Instructie voor de Boschgangers" dd. Samarang, 21 Augustus 1808, we read: "Den Lande reserveert van zich de uitsluitende behering, afvoer en debiet van het jatiehout zo van de drie hoofdsoorten:

"Jati Soengie (read *djati sungu*)
— Doerie (read *djati doreng*)
— Kapok" (read *djati kapur*)

(Staat der Nederl.-Oostindische Bezittingen, 1808—1811. 'sGravenhage, 1814, Bijlage 3, *in voce* Houtbosschen).

[2]) Over eenige Indische houtsoorten. Versl. en Meded. K. Akad. v. Wetensch. Afd. Natuurk. **9**, Amsterdam 1859, p. 44.

[3]) Bijdragen tot de kennis der Bouwkunde in Nederl.-Indië, Batavia, 1851, p. 10.

[4]) Aanteekeningen omtrent proeven, welke in 1852 in den Artillerie Konstructie-winkel te Soerabaja met djatihout genomen werden. Tijdschr. voor Nijverheid in Ned.-Indië, **2**, Batavia 1855, blz. 2; see further A. VAN LAKERVELD en G. L. BROCX, Handleiding voor bouwkundigen en industrieelen in Nederl. Oost-Indië, **1**, 's Graven-hage 1863, p. 79—80. — D. BOEKE, Het Javaansch Djattiehout beschouwd als scheepstimmerhout, Verhandel. en Berigten betr. het Zeewezen, **29**, Amsterdam, 1869, p. 171. — D. BOEKE, A Word to ship-builders about Java Teak. Nautical Magazine, **39**, London 1870, blz. 450.

[5]) Over de fossiele zoogdierbeenderen te Patihajam, Natuurk. Tijdschr. Nederl.-Indië, **14**, Batavia 1857, p. 219.

[6]) Westindische Fragmente, Botanische Zeitung, **15**, Leipzig 1857, p. 323.

as early as the following year D. Ples was able to show analyti-
cally that the secretions in djatiwood consisted chiefly of calcium-
phosphate (analysis I) [1]). Abel, who with the same object examined in
1862 the concretions in teakwood, arrived at a fairly similar result.
(Analysis II) [2]).

The experiments of either, however, did not prevent Winkelmann
from asserting 16 years later: "Im Holzparenchym sieht man kürzere
mit oxalsaurem Kalk [3]) und längere mit Luft oder Harz angefüllte
Zellen. Kieselsäure ist durch die ganze Holzmasse verbreitet [4]).

We owe the latest analyses of concretions that have come to my
knowledge to G. Thoms. The results were very similar to those of
his predecessors, so that he felt justified in saying that they were
composed of an aqueous calciumphosphate expressed in the formula:
$2CaH, HH, PO^5 + Xaq$ [5]).

I have been induced to make a new experiment by samples of
concretions, for which I am indebted to the kindness of Dr. H. C.
Prinsen-Geerligs, then of Kagok Tegal. The samples are elongated,
more or less angular, to a length of 50 cm. and of $\pm \frac{1}{2}$ to 1 cm.
diameter, the weight not exceeding 5 grms [6]). They evidently originate
from hollows that run parallel to the long axis of the stem and

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[1]) Onderzoek naar de samenstelling eener witte stof, welke zich in het hart,
alsmede in de scheuren van sommige djatiboomen afzet, waarom de boomen bij
de Inlanders den naam van Djati-Kapor dragen. Nat. Tijdschr. Ned.-Indië, 15,
Batavia 1858, p. 345—348 (extract: Examen d'une matière blanche inorganique
dans l'intérieur du tronc de l'arbre djati à Java. Journ. de Botan. Neérl. 1,
Amsterdam-Utrecht 1861, p. 135—136.

[2]) J. S. Gamble, A Manual of Indian Timbers, 2d ed. London 1902, p 533.

[3]) Julius Wiesner (Die Rohstoffe des Pflanzenreiches 2, Leipzig 1903, 2te Aufl.
p. 1005) was mistaken in presuming that G. A. Blits also has assumed the
presence of calciumoxalate.

[4]) Fremde Nutzhölzer, Die Natur. Halle a, S. 1878, p. 93. — Carl Sanio was
the first to record something about the anatomical structure of *Tectona grandis*
(Vergleichende Untersuchungen über die Elementarorgane des Holzkörpers, Bot.
Zeitung 21, Leipzig 1863, p. 110—111), J. W. H. Cordes (De Djati-bosschen op
Java, Batavia 1881, p. 22—26, pl. III, fig. 1, 2) and G. A. Blits (De anatomische
bouw der Oost-Indische IJzerhoutsoorten en van het Djatihout. Bull. van het
Kolon. Museum te Haarlem, 19, Amsterdam 1898, p. 48—50, pl. VI) gave fuller
descriptions. The latter was in a position to see the phosphate secretions as
fillings of the vessels.

[5]) Beitrag zur Kenntniss des Teakholzes (*Tectona grandis*). Die Landwirtsch.
Versuchsstationen 23, Berlin 1879, p. 68—69, 416—417).

[6]) Similar concretions may appear like fine dust, scattered in the wood as white
powdery, circular or irregular particles. On the other hand they may far surpass
as to size and circumference any known secretion in the vegetable kingdom.
W. J. Spaan has observed concretions of an arm's thickness. (Aanteekeningen over

were originally fillings of the vessels. Only few of the samples were flattened ($\pm$ 1 or 2 mm. thick); they seem to have been fillings of the clefts in the wood, evolved from the expansion consequent on the growth of the stems. On the fractures all the fragments are snow-white, somewhat cretaceous, but slightly harder ($H = 2$)[1]). The specific weight is 2.240.

In thin sections two different substances are discernible under the microscope. The one presents itself as irregular grains, clear as water, often enclosing the rest of the forest material i.e. libriform fibres. They are yellowish-brown, elongated, isolated cells, more or less curved and pointed at the extremities. The secretion from the wood very likely caused parts of the wood-tissue to be dislocated and the fibres to be deformed. The exponent of refraction is not very high and as to double refraction in polarised light, the interference colours do not rise higher than the blue of the second order. The angles of extinction were $21—22\frac{1}{2}$ degrees, but some were $31°$ or even $37°$[2]). A proper orientation could rarely be obtained owing to the lack of crystals and of distinct cleavage planes.

The second substance is turbid and finely fibrous. It consists of spherolithlike aggregate, presenting in polarised light a slanting cross, which shows that, like the first, it belongs to a clinobasic system

of crystals. The very fine needles generally have a length of 0.05 mm., though there are some of still smaller dimensions. However the fibres sometimes extend into prisms 0.2 mm. long and 0.008 mm. broad. The refraction is stronger with them than with the grains described above, but like them they are optically positive. It seems to me that the phosphate appearing in the form of aggregates is of secondary

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de in het boschdistrikt Madioen voorkomende zoogen. djativariëteiten. Boschbouw-kundig Tijdschrift. Tectona 4, Noordwijk-Weltevreden 1911, p. 473).

[1]) J. W. H. CORDES (De Djatibosschen op Java, Batavia 1881, p. 27) says on the contrary that the concretions are as a rule very hard, so that they sometimes injure the axes.

[2]) In the process of grinding thin sections some pressure on the soft grains may have been of some influence on the optic qualities.

origin i. e. a product of a morphological change of the above grains. Also from this fact it appears that the segregations sometimes, so to speak, erode the grains. It is also remarkable that those prisms and needles extinguish "einheitlich", but present aggregate polarisation, from which we conclude that they have undergone a molecular conversion and belong to a compound of only little stability.

A mechanical separation of the two substances was impracticable in consequence of their softness. While being rubbed in the mortar they were completely mixed up.

The number of analyses of concretions is not large. They have been tabulated on the next page. N°. I is made by D. Ples [1]), n°. II by Prof. Abel [2]), n°. III and IV by G. Thoms [3]), while n°. V of the substance described above was carried out in the Heidelberg Chemical Laboratory of Prof. M. Dittrich.

The analyses carried out by Ples, Abel and Thoms revealed that the concretions from teakwood consist of an aqueous calcium, phosphate, of a composition about similar to that of *Brushite* [4]), which theoretically is composed as follows:

$$P^2O^5 \quad . \quad . \quad . \quad . \quad . \quad . \quad 41.28$$
$$CaO \quad . \quad . \quad . \quad . \quad . \quad . \quad 32.55$$
$$H^2O \quad . \quad . \quad . \quad . \quad . \quad . \quad 26.17$$
$$\overline{100.00,}$$

which corresponds to the formula $HCaPO^4 + 2H^2O$.

The differences in the various results of the analyses may be accounted for by the fact that some admixtures were overlooked and also that the methods of estimating the constituents, which were then in use, involved errors that could not be avoided.

Thus far experience had taught that the composition of the secretions in plants is very constant. We need only remember the *mestika awi* (tabaschir), the *mestica kalapa*, the secretions from calciumcarbonate known by the name of cystolites, and lastly the crystallizations of calcium oxalate.

[1]) Onderzoek naar de samenstelling eener witte stof, welke zich in het hart, alsmede in de scheuren van sommige djatiboomen afzet. (Natuurk. Tijdschr. Ned.-Indië **15**, Batavia 1858, p. 345—348). The recalculation is mine.

[2]) J. S. Gamble, A Manual of Indian Timbers, New Ed. London 1902, p. 533.

[3]) G. Thoms, Beitrag zur Kenntniss des Teakholzes (Tectonia grandis), Die Landwirthschaftl. Versuchsstationen 23, Berlin 1879, p. 416—417.

[4]) G. E. Moore, On Brushite, a new mineral occurring in Phosphatic Guano, Proceed. California Acad. of Nat. Science **3**, 1867, San Francisco 1868, blz. 167—168; Amer. Journ. of Sc. (2) **39**, New Haven 1865, p. 43—44. — A de Schulten, Recherches sur le phosphate dicalcique. Reproduction artificielle de la brushite. Bull. Soc. franç. de Minéralogie **26**, Paris 1903, p. 12.

	I.	II.	III.	IV.	V.
SiO^2	—	—	—	—	0.53
P^{2}O^5	40.14	43.35	42.30	39.42	39.46
CO^2	—	0.09	—	—	0.05
Al^{2}O^3	—	—	—	—	0.05
Fe^{2}O^3	—	—	—	0.01	0.07
CaO	29.35	34.04	33.24	29.78	16.75
MgO	—	1.86	—	0.34	11.64
(NH^4)^{2}O	—	1.12	—	—	—
H^{2}O (at 100 resp. 110°)	0.50	19.54	5.92	10.40	6.11
H^{2}O (loss of heat)	28.00		18.54	12.26	25.69
Insoluble (organ. matter)	2.01	—	—	7.79	—
	100.00	100.00	100.00	100.00	100.35

It was, therefore, exceedingly striking that Dr. H. HECHT (leader of Prof. M. DITTRICH's Laboratory at Heidelberg) achieved results widely different from the four above-mentioned cases.

Leaving out of consideration the substances traced for the first time in small quantities, the high amount of magnesium oxide is most conspicuous. PLES had not found any of it, ABEL 1.86 °/, and THOMS only 0.34 °/$_0$. An increase to 11.64 °/$_0$ coincided with a decrease of calcium oxide to 16.75 °/$_0$. Since microscopical examination had already established that the secretions were to be considered as a mixture of two substances, we could hardly conclude that we had to do with a double salt viz. a calcium-magnesiumphosphate. Moreover it appeared from the calculation that the composition did not correspond with a similar compound — H^{2}CaMg(PO^2)^2 + 4H^{2}O — which would require 43.22 P^{2}O^5, 17.08 CaO, 12.28 MgO, 27.42 H^{2}O.

The presence of a mechanical mixture of a calcium- and a magnesiumphosphate or of a calcium- and a calciummagnesiumphosphate seemed to me much more plausible. On the assumption that the concretions examined by us, contain the calcium-phosphate demonstrated by PLES, ABEL and THOMS, the magnesiumphosphate may be computed from the analysis. When subtracting the 0.53 SiO^2, 0.05 Al^{2}O^3, 0.07 Fe^{2}O^3, 0.05 CO^2 present, and the 0.06 CaO required for the combination of the CO^2 the remainder will be in percentages:

$$P^2O^5 \ldots \ldots 39.63 \div 21.26 \ldots \ldots 18.37$$
$$CaO \ldots \ldots 16.76 \div 16.76 \ldots \ldots \quad —$$
$$MgO \ldots \ldots 11.68 \ldots \ldots \ldots \ldots 11.68$$
$$H^2O \ldots \ldots 31.93 \div 13.47 \ldots \ldots 18.46$$
$$\overline{51.49 \qquad\qquad 48.51}$$

The percentages of the composition of magnesiumphosphate will then be

$$P^2O^5 \ldots \ldots 37.88$$
$$MgO \ldots \ldots 24.07$$
$$H^2O \ldots \ldots 38.05$$
$$\overline{100.00}$$

which fairly correspond with the formula

$$HMgPO^4 + 3^1/_2\, H^2O$$

which requires

$$P^2O^5 \ldots \ldots 39.58$$
$$MgO \ldots \ldots 22.50$$
$$H^2O \ldots \ldots 37.92$$
$$\overline{100.00}$$

In criticizing the above calculation we should bear in mind that a complete correspondence with the results of the analysis cannot be expected on account of our ignorance of the influence of small quantities of SiO^2, Al^2O^3 and Fe^2O^3. In part at least they originate from the enclosed fragments of woodtissue, which apart from that also contains P^2O^5, CaO and MgO.

The magnesiumphosphate in the above calculation is unknown in nature [1]; but there is another reason to assume that the second substance is not a magnesiumphosphate, but a calcium-magnesium-phosphate, viz. the fact that the original calciumphosphate does not nearly make up half the concretions. It follows then that calcium-oxide must also be present in the fibrous aggregates.

The answer to the second question viz. to what the considerable difference in the chemical composition of the concretions is to be attributed, is given in the ash-analyses tabulated below; N° VI (of the sapwood) and VII (of the heartwood) we owe to R. Romanis [2]) and those of VIII to G. Thoms [3]).

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[1]) We only have *Bobierrite* $Mg^3(PO^4)^2 + 5\,H^2O$ with 40,21 P^2O^5, 34.28 MgO, 25,51 H^2O and *Newberyite* $HMgPO^4 + 3\,H^2O$ with 40,71 P^2O^5, 23,14 MgO, 36,15 H^2O.

[2]) J. S. GAMBLE, A Manual of Indian Timbers, London 1902, p. 532.

[3]) Beitrag zur Kenntniss des Teakholzes, Die Landwirtschaftl. Versuchsstationen 23, Berlin 1879, p. 419.

As could be expected the constituents of the secretions are also found in the ash of the wood of varieties of *Tectona grandis* not belonging to *djati kapur*. Furthermore, if we reflect that in the sappy

	VI.	VII.	VIII.
SiO_2	23.36	32.69	24.98
P_2O_5	31.97	27.42	29.61
SO_3	—	—	2.22
Fe_2O_3	2.42	1.79	0.80
CaO	7.35	11.80	31.35
MgO	30.57	21.97	9.74
K_2O	1.75	1.51	1.47
Na_2O	2.58	2.82	0.04
Cl	—	—	0.01
CO_2	—	—	0.01
	100.00	100.00	100.23

outer layers of the wood concretions never occur, though their constituents are present, we may safely conclude that there must be some relation between those secretions and the decrement of the amount of sap.

The amount of phosphoric acid in the 3 analyses does not vary considerably; there is a difference with respect to calcium- and magnesium oxide. A comparative index is given by the analyses of ROMANIS, because the heartwood and the sapwood were examined inter se. With reference to this it should not be forgotten, that the heartwood yielded 1 %, the sapwood only 0.74 % of ash. In this way the larger amount P_2O_5 (31.97 %) in the sapwood against 27.42 % in the heartwood, is only an overestimation, for the wood it is no more than 23.66. In the same way we get 5.44 instead of 7.35 % of CaO and 22.62 instead of 30.57 % of MgO. It will be seen that the CaO-content of the heartwood (11.80 %) is more than twice that of the sapwood (5.44 %), which readily accounts for the secretion of phosphate; it does not, however, point to the causes of this secretion, for they are the rule with *djati kapur* and the exception with other varieties. Apparently softness and less solidity of the wood tissue go together with secretions, which result from them. In the analysis by THOMS VII we notice a MgO-content of only 0.94 %

against 31.35 of CaO. With reference to this it is obvious that the phosphate engendered contained chiefly only Ca, while from the ash analysis the conclusion might be drawn that one tree absorbs more Mg than the other.

I think it is in keeping with the general rule to state that the concretions have originally been made up of calciumphosphate, which afterwards was gradually changed under the influence of a detached organic magnesiumsalt. This change caused the formation of magnesiumphosphate, which is more difficult to dissolve [1].The clear crystal grains could then be looked upon as the still untouched remainder of the calciumphosphate. Without such a metamorphosis the two phosphates must have been secreted simultaneously, which does not seem probable to me. Still less can there be any question of periodicity in the secretion of the two phosphates, because this would have to be proved by a zonary structure, which could not be detected in any of the preparations. To solve the question we need a larger amount of material. I also deem it necessary to analyse, besides the concretions themselves, also the wood of the stems from which they originate.

Tectona grandis is the greatest phosphorus devourer known, it would, therefore, be interesting to find out whether on that account it also spoils the soil [2]). The amount of phosphoric acid it absorbs, may be computed from the annual amount of djati wood, cut in Java. From 1902 to 1915 (inclusive) it was

$$3.148950 \text{ M.}^3 \text{ of timber and}$$
$$11.035108 \text{ M.}^3 \text{ of firewood [3]),}$$

representing respectively a weight of 2074.347000 kg. [4]) and 4855.447740 kg. [5]).

According to ROMANIS heartwood yields 1 °/₀ and sapwood 0.74 °/₀

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[1]) I do not think it at all improbable that such a change can be effected experimentally, viz. through impregnation of squashed cell-sap of Mg-rich teak-trees into normal concretions of calciumphosphate.

[2]) The question whether djati is a spoiler of the ground has given rise to some controversy, however, only with respect to the slight formation of humus in the forests. (J. C. CLAESEN, Iets over djati. Boschbouwkundig Tijdschr. Tectona **1**. Noordwijk-Weltevreden 1908—9, p. 166. — H. J. KERBERT, Is djati grondbederfster? Ibid. **1**. 1908—9, p. 301—304; **2**. 1909—10, p. 44—46. — J. C. CLAESEN. Antwoord aan den heer KERBERT. Ibid. **1**, p. 575).

[3]) Verslag van den Dienst van het Boschwezen in Nederl.-Indië over het jaar 1915. Batavia 1916, p. 18.

[4]) The average specific weight was fixed at 0,66.

[5]) Firewood is calculated by the running meter. It consists of branches and other debris of wood, leaving empty spaces that were subtracted as $1/3$.

of each [1]). The timber may be chiefly considered as heartwood, so that the amount mentioned above must yield 20.743470 kg., containing 5.694082 kg. of phosphoric acid. To prevent overestimation the firewood was taken for sapwood. A weight of 4855.447740 kg. furnished 35.930313 kg. of ash containing 11.486921 kg. of phosphoric acid. The total amount of P^2O^5 of which the ground of the djati-forests were deprived in the years 1902—1915 is 17.181003 kg. or a yearly average of 1.227212 kg. on a surface of 713474 H.A. [2]) or 1.72 kg. per H.A.

As known, *Tectona* thrives on any soil, even a poor one. In the island of Java by far most of its forests lie on limemarls, which are reckoned to belong to phosphoric acid poor soils. It has to surmount the difficulty of procuring the required amounts of P^2O^5 by means of its roots. In its youth this is achieved by a strong taproot. H. J. KERBERT established that the root of a 31 month-old tree had already reached the height of 140 cm. [3])

When the tree has reached the polewood stage the taproot dies down, while the lateral roots develop into a strong root-system, enabling the tree to draw the available foodstuffs from the soil in an effectual way.

According to S. H. KOORDERS and TH. VALETON djatitrees $\pm$ 25 m. high, had lost the taproot, on the other hand numerous lateral roots, of 3 m. length at the most, branched out considerably, to 3 m. round about the stem [4]).

As yet it has not appeared that the grounds in Java covered with djati, have been explored from time immemorial. Sometimes [5]) the ground is said to be "tired" of djati, but nobody has as yet tried to ascertain whether want of phosphoric acid is the cause of it.

We wish to emphasize the circumstance that the above mentioned 1227112 kg. of phosphoric acid, withdrawn every year from the grounds, is not really a loss, but only a displacement of P^2O^5. Only such a quantity of phosphoric acid as is comprised in the teakwood exported, may be called a real loss.

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[1]) J. S. GAMBLE. A Manual of Indian Timbers. New Ed. London 1902, p. 532.

[2]) Verslag van den Dienst van het Boschwezen in Nederlandsch-Indië over het jaar 1915. Batavia 1916, p. 1. It matters little that formerly the surface was thousands of hectares smaller.

[3]) Worteldiepte van de djati. Boschbouwkundig Tijdschr. Tectona 1. Noordwijk-Weltevreden 1908—9, p. 340.

[4]) Bijdrage N°. 7 tot de kennis der boomsoorten op Java. Mededeelingen uit 's Lands Plantentuin N°. XLII. Batavia 1900, p. 166.

[5]) A. E. J. BRUINSMA, Opmerkingen van een oudgediende. Boschbouwkundig Tijdschr. Tectona 3. Noordwijk—Weltevreden 1911, p. 5.

From 1903 to 1915 Java exported 598846 m³, containing 1083743 kg. of phosphoric acid, which signifies an annual loss of 83365 kg,, a trifle, indeed, as compared with the enormous quantities discharged into the sea with the silt of rivers [1]).

As observed before the teak-tree requires much phosphoric acid. Contrariwise it thrives on any soil whatever — as far as its chemical composition is concerned [2]). With a view to the calcareous secretion it was obviously supposed that the appearance of djati-kapur was associated with the nature of the soil. THOMAS HORSFULD, who was the first to discuss this point, thought that the poor lime-containing territories yielded the best trees, whereas djati-kapur is more often found in the fertile districts [3]).

This view is supported by what W. J. SPAAN wrote concerning the forests of Puger (resid. of Besuki): "There it appeared that djati-kapur, with a very high lime-content, occurred in large quan-

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[1]) Reliable data we have none, and they will not be at our disposal within a near date. The following, however, tends to show what quantities of phosphoric acid are concerned. According to L. RUTTEN about 9600,000,000 k g . of silt are transported anually from the Seraju-territory in the island of Java (Over denudatie-snelheid op Java. Verslag gewone Verg. Wis- en Natuurk. Afdeeling K. Akad. v. Wet. **26.** Amsterdam 1917/18, p. 930 table). According to JUL. C. MOHR (Over het Slibbezwaar van eenige rivieren in het Serajudal. Meded. uitgaande van het Dep. van Landbouw N⁰. 5. Batavia 1908, p. 79) the average content of P_2O^5 in this silt is 0,753⁰/₀, so that every year 72,288000 kg. of phosphoric acid is taken from the said territory, which means 267,7 kg. per H.A. Compared with this amount the loss of the grounds of the djatiwoods in consequence of the withdrawal of 1,72 kg. of wood per H.A. is trifling. The loss of phosphoric acid resulting from the denudation process is only a seeming loss, since the silt, which is richer in P_2O^5 than the primitive rocks and is transported to the sawahs by means of irrigationworks, imparts P_2O^5 to the grounds and thus makes them richer. (L. G. DEN BERGER, Landbouwscheikundige onderzoekingen omtrent irrigatie op Java. Delft 1917. Proefschrift, p. 82, 83, 97, 98). In the Kali Samiran for instance they found: silt 0,051, 0,055, 0,043, 0,048 ⁰/₀ of P_2O^5 (p. 82); on the other hand in the ground of Bolgi only 0,022 and of Kolpandjong 0 017 ⁰/₀ of P_2O^5 (p. 85), the water of that river contains only traces.

Seraju-territory ± 2700 km²., Java ± 125,500 km²., so that the annual loss will be 2621,534815 kg. of P_2O^5.

[2]) Much more selective is *Tectona* with regard to the physical condition of the soil. It requires as BRANDIS positively says "perfect drainage and dry subsoil" (l.c. p. 358).

The withdrawal of phosphoric acid from the soil of Java is enormous in relation to those in temperate climates. The Elbe in Bohemia e.g. withdraws yearly $1\frac{1}{2}$ million kg. of P_2O^5 according to BREITENLOHNER (Verhandlg. k. k. geolog. Reichs-anst. Wien 1878, p. 175), which signifies a loss of only 0,031 kg. per H.A.

[3]) C. L. BLUME, l.c. p. 44.

tities on the fertile ground, periodically very moist and black, at the foot of the Watangan range, whereas higher up on the rocky slopes of this tertiary hill, teakwood is of much better quality [1]).

C. G. von Dentzch, on the other hand reported that most of the trees cut in the residence of Rembang (where limestone and marl predominate) belong to djati-kapur [2]); this at least was the case with the trees used in the "Artillerie-construktiewinkel" of Surabaya. On the basis of the fact that this variety is found on the white lime-marl-formation at Surabaya and Rembang, F. Junghuhn asserted positively that it originated from the nature of the soil [3]). In his account P. F. H. Fromberg had in mind the phosphoric acid content of the soil rather than the lime. According to him this content must be comparatively high in places where the teak-tree grew [4]). G. Thoms went even so far as to think that under the teak forests phosphorite-beds were to be found, which has not been proved [5]).

According to J. W. H. Cordes teak forests thrive best "where the soil is rich in various lime-compounds, but he admits that also volcanic grounds produce good teak trees [6]). H. J. Kerbert never met with such a luxuriant growth of the teak as in Japara ... on light volcanic grounds that differ in nature entirely from the typical teak-forest grounds [7]).

Statistic data with reference to the number of the hewn trunks of *djati-kapur* enabling us to compare them with other varieties, are missing altogether. Certain it is, anyhow, that the majority do not belong to the first mentioned, variety. According to P. van Rees it is found and used most after the *djati sungo* is perhaps

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[1]) Aanteekeningen over de in het boschdistrict Madioen voorkomende Djati-variëteiten. Boschbouwkundig Tijdschr. Tectona 4. 1911, p. 473.

[2]) Aanteekeningen omtrent proeven welke in 1852 in den Artillerie-Constructie winkel te Soerabaja met djatihout genomen werden. Tijdschr. voor Nijverheid in Ned.-Indië 2. Batavia 1852, p. 2.

[3]) Over fossiele zoogdierbeenderen te Patihajam. Natuurk. Tijdschr. Ned.-Indië 14. Batavia 1857, p. 219. — Ch. C. Lugt attributes the lime-content 'aan sommige groeiplaatsen." (Het boschbedrijf in Ned-Indië. Haarlem 1912, p. 20).

[4]) Witte stof in de djatikapur. Natuurk. Tijdschr. Ned.-Ind. 16. 1858—59, p. 186.

[5]) l.c., p, 427.

[6]) 'De Djati-bosschen op Java". Batavia 1881, p. 131. — After a report by Dietr. Brandis the teak tree is found in British India on all sorts of grounds, as basalt, granite and limestone. To the latter belong i.a. the excellent forests in the Thoungyeen-district in Tenessarim (The Forest Flora of North-West and Central India. London 1874, p. 356).

[7]) 'Is de Djati grondbederfster?" Boschbouwk. Tijdschr. voor Nijverheid en Landb. Tectona 1. Noordwijk-Weltevreden 1908—9, p. 303.

owing to the smaller working qualities of teakwood as timber [1]).

It must be admitted, therefore, that *djati kapur* is not restricted to lime- and marl-grounds, also that not all trees growing on those grounds belong to this variety [2]). Other influences must be exerted here. To answer this question it is first of all necessary to ascertain whether *djati kapur* may be called a variety by itself or whether we have to do here only with an aberration, forming under certain circumstances only. According to KOORDERS and VALETON *djati kapur* can only be recognized in the wood and not in the stem, like other varieties of Tectona [3]).

However, P. VAN REES already reported: "The outward marks of identity are according to the Javanese, the smaller, thinner yellowish leaves and the finer bark" [4]), but he added: "thesemarks, however are deceptive, the true characteristics being found inside" [5]). W. L. STURLER does not distinguish *djati kapur* from other varieties only by the bark, the nature of the wood, the shape and the colour of the leaves. H. J. SPAAN also says that some wood-cutters can tell from the outside of a tree that it is *djati kapur* namely from "the bark, the stem and the leaves" [6]), What P. VAN REES writes further about the fruits is also worth noticing: "In the exceed-ingly small fruits of this sort fine limeveins are said to have been detected" [7]).

Whether this is really the case, has never been examined, nor have any efforts ever been made to ascertain by sowing-experiments whether or no from these fruits representatives of *djati kapur* may

[1]) Beredeneerde catalogus van houtsoorten op Java. Tijdschr. voor Nijv. en Landb. in Ned.-Indië **7**. Batavia 1861, p. 333.

[2]) M. BÜSGEN also thinks that the commercial reputation of Java-teak is based on wood from *djatikapur* (Die Eigenschaften und Production des Java-Teak oder Djati. Beiheft zum Tropen pflanzer **8**, N⁰. 5. Berlin 1907, p. 369). P. GEESINK also says that in 1905 and 1906 much wood was exported from Java, totally unfit for foreign markets (Staatsexploitatie van Djatibosschen op Java.... Tijdschr. voor Nijv. en Landb. in Ned.-Indië **75**. Batavia 1907, p. 133).

[3]) To solve the question of the widely differing amount of magnesiumoxide a larger number of ash-analyses of *Djatikapur* as well as of soilsamples from the places where they are taken from, seems to be required.

[4]) Bijdrage N⁰. 7 tot de kennis der boomsoorten op Java. Mededeelingen uit 's Lands Plantentuin N⁰. XLII. Batavia 1900, p. 170.

[5]) Beredeneerde catalogus der houtsoorten op Java. Tijdschr. voor Nijverheid en Landb. in Ned.-Indië **7**. Batavia 1861, p. 333.

Beschrijving der houtsoorten in Ned. Oost-Indië, Tijdschr. Maatschappij voor Nijverheid (3) **7**. Haarlem 1866, p. 29.

[6]) Aanteekeningen over de in het boschdistrict Madioen voorkomende zoogen. djativariëteiten. Boschbouwk. Tijdschr. Tectona **4**. 1911, p. 473.

[7]) l.c., p. 334.

grow up. The objection that a result from this experiment cannot be obtained before a hundred years later, cannot be a reason for not trying it now. It should be attended, however, with a second experiment, viz. of planting seedlings of other djati-varieties on a patch of lime- or marlgrounds, in order to ascertain whether stems of djati-kapur may be grown from them [1]).

Lastly the question may be asked: what is the fate of the phosphates secreted in the stems of *djati kapur?* The stems, the branches and the leaves rotting in the forests return in the compounds of phosphorus present in the tissue, to the ground in the form of wood ashes. In this process the concretions also must come to the same place, though it has not been recorded anywhere that they were found there.

A regular forest-administration will cause them to be transported elsewhere together with the stems in which they are shut up. It is obvious, therefore that the quantity of concretions remaining on the forestgrounds cannot be very large. Moreover most of them are of small dimensions and very soft, so that they readily fall to pieces and will be transported farther in the wet season, so that only very few will be left behind. The inevitable decomposition-process is much slower of course, since though it may be true that calcium-phosphate is assimilated by the root of the plant, atmospheric influences affect it in a much smaller degree, than is the case even with a number of silicates. I, therefore, deem it very probable that the numerous kidney-shaped concretions, found near Solo in the territory of Surakarta in the clay overlying the tertiary sediments, may be looked upon as a remnant of the secretions formed in the *djati kapur,* as assumed by R. D. M. Verbeek [2]). An analysis by J. G. Kramers led to the following results:

$$
\begin{array}{ll}
SiO_2 & \dots\ 8.81 \\
P_2O_5 & \dots\ - \\
CO_2 & \dots\ 38.15 \\
Fe_2O_3 + Al_2O_3 & \dots\ 1.92 \\
CaO & \dots\ 48.29 \\
H_2O & \dots\ 1.15 \\
\hline
& 98.32
\end{array}
$$

[1]) H. ten Oever (Cordes: De Djatibosschen op Java, Boschbouwk. Tijdschr. Tectona 9. 1916. Batavia 1917, p. 869) has already pointed out that only a thorough investigation of the so-called djati-varieties with respect to their being true to seed will enable us to settle this question.

[2]) R. D. M. Verbeek en R. Fennema. Geologische beschrijving van Java en Madoera 1. Amsterdam 1896, p. 209, 325.

which shows, that phosphoric acid had disappeared completely, which struck VERBEEK also and of which no other instance is recorded, for even there where a conversion of phosphate to carbonate has taken place, large quantities of phosphate were left [1]. Calcium-phosphate, it is true, is readily assimilated by the roots of plants, but the analysing influence of circulating waters is much smaller. Besides, the shape of those concretions is quite different from those that are found in the stems of *Tectona*.

[1] JUSTUS ROTH. Allgemeine und chemische Geologie 1. Berlin 1879, p. 92—94, 211.

Geology. — *"On the Volcanoes in the Island of Tidore (Moluccas)"*. By Prof. A. WICHMANN.

(Communicated in the meeting of December 28 1918).

The finest view to be had from the landing stage of the capital of Ternate is that of the slender peak of Tidore, the most regular volcanic cone of the Moluccas, at a distance of about $13\frac{1}{2}$ km. Directly the voyager arrives, he becomes aware that the peak is not isolated but that some of its slopes are concealed by some smaller mountains, stretching as far as the North Coast of Tidore. A capital picture of it is given in the publication of the Siboga-Expedition, which is reproduced below [1]). (Fig. 1). A graphical plan of it has also been made by F. H. H. GUILLEMARD [2]). The volcano affords quite a different aspect, when one approaches the island from the south. No other hill-formations, either from this or from the West-

Fig. 1. The Island of Tidore, seen from the N.-W.

side, hinder [3]) the view of the volcano, which rises so gently from

[1]) MAX WEBER. Introduction et description de l'expédition: Siboga-Expeditie 1. Leiden 1902. p. 63.

[2]) "The Cruise of the Marchesa to Kamschatka and New-Guinea". 2. London 1886, p. 228. K. MARTIN's representation (Reisen in den Molukken. Geolog Theil. Leiden 1903, p. 59) is less accurate.

[3]) A. R. WALLACE mistakenly speaks of rugged-looking hills south of the peak ("The Malay Archipelago" 2. London 1869, p. 24. — A. R. WALLACE—P. J. VETH. "Insulinde" 2. Amsterdam. 1871, p. 30).

As early as 1856 P. BLEEKER wrote: ("Reis door de Minahassa en den Molukschen

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the beach. From the east side a clear survey of the adjoining mountains may be obtained. R. D. M. VERBEEK has endeavoured to represent their relative positions in a profile [1]) Fig. 2.

It will be seen that after peak (4) — called by the natives Kiè Matubu — comes a mountain (3), 903 m. high, which is followed again directly by another (2), 661 m. high. The series is concluded in the North by a cone (1) with two peaks, the southern emerging 665 m. above the sea-level. VERBEEK considers this cone to be a

Fig. 2. The Island of Tidore, seen from the E.

collapsed volcano and has tried to give a reproduction of its original shape.

The long felt want of a topographical map of the island of Tidore, has recently been supplied by a native surveyor on the instruction of the Topographical Institute [2]). His sketchmap represents in a masterly way the Tidore mountain-building, by which we are enabled to judge of the accuracy of VERBEEK's reproduction.

C. G. C. REINWARDT was the first to ascend the Kiè Matubu — the peak proper — from the capital of Soa Siu situated on the South-east side, on August 29, 1821. It was then discovered that

Archipel" 1. Batavia 1856, p. 212): "The southern half of the island is formed "entirely by the peak of Tidore, a regular cone. The northern half on the "contrary consists of a mountainous country, a wilderness of volcanic nature, only "a link of the chain of volcanic mountains that surround Halmahera to the West." — Concerning the last observation, it is scarcely to be doubted that the chain of volcanoes in the Moluccas is continued first of all from the volcano of Maftutu to the island of Maitara and thence again in northern direction to the islands of Ternate and Hiri. Only then does it turn eastwards toward Halmahera.

It may be, though, that, starting from the volcano of Maftutu, the chain also branches off towards Halmahera, in north-eastern direction to the bay of Dodingah. This extension, according R. D. M. VERBEEK (Molukken-Verslag. Jaarboek van het Mijnw. Ned.-Indië 37. Wetensch. ged. Batavia 1908, p. 162) is an old fallen-in volcano with a radius of at least 5 km. According to E. GOGARTEN (Geologie van Noord-Halmahera. Verhandel. Geolog. Mijnbouwk. Genootsch. 2. 's-Gravenhage 1918, p. 269) andesite breccia and coarse-grained tuffs, in which fragments of white pumicestone, are found also on the other side of the bay in the bay of Bobane.

[1]) Molukken-Verslag. Jaarboek v. h. Mijnwezen in N. O. I. 37 Wet. ged. Batavia 1908, p. 144—146; Bijl. V, fig. 137.

[2]) Sketch-map of the islands of Tidore and Maitara 1 : 20000. Batavia 1916. Topogr. Institute.

the North-West side of the crater-rim had been broken through. The height of the western rim was established at 5598 ft. (5435 rh. ft.). No fresh traces of volcanic action were detected in the densely wooded crater. According to REINWARDT the prevailing rock of the mountain, as well as of the whole island, is basalt [1]).

Of the ascent, performed in 1841 by the late E. A. FORSTEN, no further information has reached us beyond the fact that he determined the height of the mountain at 5376 rh. ft. [2]). Besides by the native surveyor (in 1915), the volcano has since that time also been ascended on Sept. 9, 1903 by Captain G. J. J. DE JONGH and a patrol of 19 fusileers from the southside. From the notes the latter was kind enough to send us, we could infer that the summit had not undergone any real alteration since REINWARDT's ascent. The width of the crater was approximately equal to that of the peak of Ternate, but the walls were considerably less steep and densely wooded.

It should be borne in mind that the height of the summit was determined only from the sea, except in the year 1915. The determinations are the following:

C. G. C. REINWARDT 1821 1702   m.
E. A. FORSTEN 1841 . . . . 1687,26 ,,
Challenger-expedition 1874 1798,3   ,, [3])
Siboga-expedition 1899 . . . . . . , 1754   ,, [4])
R. D. M. VERBEEK 1899 . . . 1717 and 1724   ,, [5])
Native Surveyor 1915 1730   ,,

The last determination must, no doubt, be nearest to the truth.

As REINWARDT could observe, explosions are not likely to have taken place in historic time. True, in the oldest picture of the volcano, in the work of J. TH. and J. J. DE BRY, a smoke-cloud is seen above the summit, but the text does not make mention of any volcanic activity [6]).

J. MERCALLI [7]) and K. SCHNEIDER [8]) have recorded an eruption of

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[1]) Reis naar het oostelijk gedeelte van den Indischen Archipel in het jaar 1821. Amsterdam 1858, p. 497—501.

[2]) P. MELVILL VAN CARNBÉE, Over de hoogte der bergen van den Oost-Indischen Archipel. Tijdschr. voor Nederl.-Indië 1844. 1. p. 545.

[3]) Report on the Scientific Results of the Voyage of H. M. S. CHALLENGER. Narrative 1. 2. London 1885, p. 594.

[4]) L.c. p. 61.

[5]) L.c. p. 149.

[6]) Indiae orientalis 8. Francofurti 1607, p. 23, tab. XIII, XVIII.

[7]) I vulcani attivi della terra. Milano 1907, p. 310.

[8]) Die vulkanischen Erscheinungen der Erde. Berlin 1911, p. 242.

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the year 1608 (in the latter half of June or the beginning of May), although some time before their publication the report, upon which their communication was founded, proved to be false [1]). It came to pass in the following way. In the original edition of the work of A. Fr. Prevost [2]) we are told that the said eruption was witnessed on the second voyage of Paulus van Caerden. However, the voyager states in his narrative that the volcano that was active late in the evening (during the first watch) of the 18th of July, was the peak of Ternate [3]). Even Prevost's rectification in the Hague-edition of his work: "Dans l'édition de Paris il y a Tidor, ce qui est une faute" was of no avail, for Alexis Perrey had copied the erroneous information from the first edition and communicated at the same time the true fact regarding the eruption of Ternate [4]). From his notes both communications passed into the above-mentioned works of Mercalli and Schneider.

Violent shocks of earthquake were felt in Ternate and in Tidore on the 14th of July 1855. In the latter island 25 houses collapsed, which cost the lives of 24 men, while four more were killed [5]) by blocks of rock sliding from the Dojado [6]) hill.

Subsequently it was reported in 1856 that: "prognostics had been observed of an eruption of the peak in the near future" [7]). What these indications were, we are still to learn; at all events the anti-cipated eruption stayed away. The landslip that had occurred in June 1857 north of the capital Soa Siu [8]) was not generated by volcanic activity any more than the torrent of mud of the 6th of September 1866, that rose at the slope of the peak above the campong

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[1]) A. Wichmann. Der Wawani auf Amboina und seine angeblichen Ausbrüche. Tijdschr. Nederl. Aardr. Gen. (2) 16. 1899, p. 16.

[2]) Histoire générale des Voyages 8. Paris 1750, p. 385.

[3]) Loffelijcke Voyagie op Oost-Indien. Begin ende Voortgang van de Vereenigde Geoctroyeerde Oost Indische Compagnie 2. Amsterdam 1646, N⁰. 14, p. 47. — F. Valentijn. Oud en Nieuw Oost Indien 1. 2. Dordrecht—Amsterdam 1724, p. 5.

[4]) Histoire générale des Voyages 10. La Haye 1753, p. 385.

[5]) Aardbevingen in den Indischen Archipel. Natuurk. Tijdschr. Ned. Ind. 9. Batavia 1855, p. 519. — P. van der Crab (De Moluksche Eilanden. Batavia 1862, p. 290) reports that 32 persons were killed by the sliding rocks F. S. A. de Clercq (Bijdragen tot de kennis der residentie Ternate. Leiden 1890, p. 69, aant. 1) erroneously fixes the date on the 6th of Sept. 1866. Van der Crab's work had already appeared in 1862.

[6]) The Dojado hill is situated on the south-east base of the Maftutu about 1,6 km. south of Akè Sahu.

[7]) Fragment uit een reisverhaal. Tijdschr. v. Ned. Indië 1856. 1, p. 425.

[8]) J. H. Tobias. Aardstorting op Tidore. Natuurk. Tijdschr. Ned. Indië 15. Batavia 1858, p. 352—358.

Tugoriha, and, according to F. S. A. DE CLERCQ resulted from a landslip consequent on heavy rains [1]).

The communication given by the "Aardrijkskundig en Statistiek Woordenboek van Nederlansch Oost-Indië" that from time to time steam is emitted by the crater [2]) has been discredited by F. S. A. DE CLERCQ [3]).

The peak with its broad base has encroached the whole of the southern part of the island. We could say $^2/_3$ of the whole island, but for a considerable deviation from the regular cone-shape, brought about by the formation of three associated cones by subsequent eruptions, the most eastern of which is 820 m. high and is called Kiè Kitji [4]). In VERBEEK's reproduction this is vent N°. 3 to which by him a height of 903 m. [5]) is assigned.

Behind the Kiè Kitji and to the west of it rises a nameless summit whose height has not been mentioned; judging from the curves of height it must be 870 m. Due North lies the Buku Nagafura (830 m.), which — like the preceding — will be visible from the sea. Deep ravines run down from the three summits; no doubt these formations must be considered as parasitic cones.

Contiguous to the Buku Tagafura are two summits, at a distance of only 400 m. from each other, the Buku Gulili (485 m.) and the Buku Tululu (500 m.). Together they correspond to VERBEEK's vent of eruption 2, whose height is estimated at 600 m.

With respect to VERBEEK's fourth vent of eruption, which we will call the volcano of Maftutu, his map brought us a surprise. In fig. 3 we give part of the map on a small scale. As will be seen directly, what VERBEEK conceived intuitively, has proved to be correct. He could see only the elevations of the eastern crater-rim, viz. the Bulu Pandanga (570 m.) the Bulu Mafu Murot (560 m.) and the Tasuma Mabulu (500 m.). The highest summits visible from the sea in the neighbourhood of the coast, rise higher than the west-rim. They are the summits of Buku Kabahoso, one of which, towards the south, rises to 680 m.; the others only to 570 m.

On the caldera, 325 m. above the sealevel rises the Bulu Maitara

[1]) L.c. p. 68—69.

[2]) 3. Amsterdam 1869, p. 956.

[3]) "Bijdragen tot de kennis der residentie Ternate." Leiden 1890, p. 68, aant. 4.

[4]) This volcano and the Kiè Matubu are the only mountains that the Tidorese deem worthy to be called so; the others are in their eyes only hills: "buku".

[5]) We cannot say which estimation is the more reliable, until we know in what way the surveyor performed his measurement.

(570 m.) [1]) besides two lower cones. The smaller (eastern) part of the floor of the crater is flat and partly marshy. The caldera is not quite circular, its diameter is in E.W. 2.8 km. Its depth is 150 m., the average height of the crater-rim 535 m. From the site of the summit of the Bulu Maitara it appears that the centre of eruption has shifted ± 50 m. westwards.
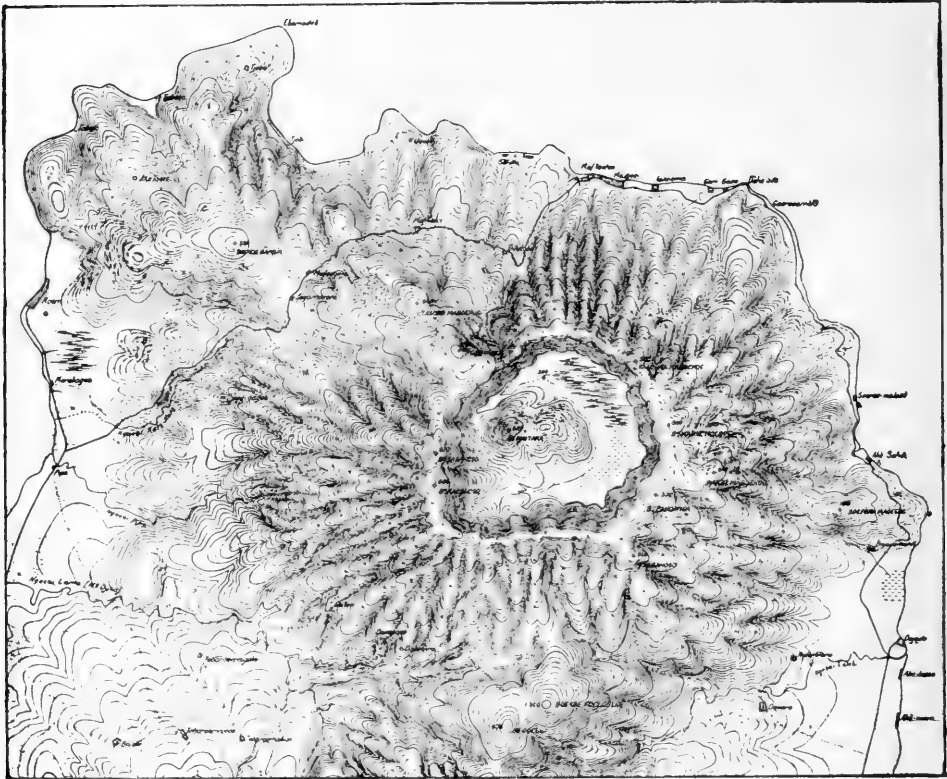
Fig. 3. The volcano of Maftutu.

The latest indication of the volcanic activity of this mountain of craters is a hot spring, found at the east-base near the campong Akè Sahu, close to the beach. According to C. G. C. REINWARDT it has a temperature of 90° F. (32° C.)[2]). It has also been visited by H. A. BERNSTEIN[3]) and H. VON ROSENBERG[4]). R. D. M. VERBEEK[5])

[1]) To be distinguished from the volcano of the island of Maitara, which is situated 5.6 km. to the West of Bulu Maitara.

[2]) L.c p 496.

[3]) Mededeelingen nopens reizen in den Indischen Archipel. Tijdschr. voor Ind. T. L. en V. 17. Batavia 1869, p. 79.

[4]) "Reistochten naar de Geelvinkbaai." 's-Gravenhage 1875, p. 11. — Der Malayische Archipel. Leipzig 1878, p. 403.

[5]) L.c. p. 146.

discovered that it rises from andesite. At the northern base on the beach near the kampong Maftutu I saw on the 1st of September 1903, some cold springs appear from under the yellowish brown tuff and below the sealevel.

Beyond the northwest side of the outer crater-rim rises the Kota Mum, which is apparently the vent[1]) indicated by Verbeek as the north rim of the large crater-wall. Evidently it is from this vent that the lavastreams were ejected that were denuded at the western side of the north coast of Tidore. Further to the northwest follows the Tarobo Mabulu (540 m.) and the Bulu Gambir (320 m.) The order of the vents of eruption will be 4, 3, 1, and 2, while it is still an open question whether 3 is older than 1.

Concerning the rocks we can still add that Reinwardt considered the unweathered material of the peak and of the whole island to be basalt[2]). J. W. Retgers determined[3]) a fragment from an obsidian-like lavastream near Soa Siu as hypersthene-andesite. Another piece of unknown origin proved to be pyroxene-andesite. The lavastream at the south base near campong Seli also belongs to this group of rocks, according to Verbeek[4]). Nothing is known as yet concerning the petrographical character of the volcanoes lying between the peak and the volcano of Maftutu. But near Akè Sahu at the east base of the above-mentioned mountain Verbeek found the following profile: Substratum of $1\frac{1}{2}$ m of andesite, upon this $1\frac{1}{2}$ m of tuff, then $^1/_2$ m of yellow tuff and superposed on this 6 or 7 m of pumicestone-tuff[5]).

The above-mentioned, horizontally stratified, yellowish brown tuff near the campong of Maftutu proved to be an andesitic tuff, easy to pulverize. The numerous rock-fragments enclosed in it are gene-rally not bigger than grains of sand; only some fetch a diameter of $^1/_2$ c.m. Under the microscope the fragments present structures that prove them to belong to several varieties of andesites, mostly to the pyroxene-andesites. Some, however, contain barkevitic amphi-bole. The groundmass of these rocks is felsite-like or hyaline. In the latter case it also encloses numerous angite-microlites. The fel-spars — mostly plageoclases — are most often quite fresh and clear as glass. The cement consists of a powdery and highly decom-posed débris of rocks, mixed with numerous brownish-yellow par-

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[1]) L.c. Bijlage V, fig. 128.

[2]) L.c. p. 499.

[3]) Mikroskopisch onderzoek van gesteenten uit Nederl. Oost-Indië. Jaarboek van het Mijnwezen in N. O. I. 24. Wet. gedeelte. Amsterdam 1895, p. 120.

[4]) L.c. p. 251.

[5]) L.c. Bijlage V, fig. 129.

ticles of ironhydroxide, which give the peculiar colour to the rock. The cement contains moreover numerous splinters of felspars and augites, besides granules of black iron-ore. All this shows that this tuff cannot be solidified ashes, but is to be looked upon as a con-glomerated product of decomposed volcanic material.

Farther to the east, near the campong Sekèta I found solid ande-site like that of which the campong Tjobo is made up, while in the small bend near the said campong again andesite-tuff has been laid bare. We can add also that on the North-West side of the island, near Tandjung Rum, hornblende-, augite- and augite-andesite are found [1]).

In conclusion let it be stated that, when, in 1858, J. H. CROOCKEWIT picked up a piece of mica-schist behind Humboldt Bay in New Guinea, Prince Amir of Tidore, who saw him do so, was induced to observe: "that it was not at all of rare occurrence in Tidore" [2]). Still, from this pronouncement we can infer only that some lustrous mineral is not rare in the rocks of that island.

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[1]) A. WICHMANN. "Nova Guinea" 4. Leiden 1917, p. 45.

[2]) "Oppervlakkige geognostische schets der bezochte punten op de zuid-, west- en noord-kusten van Nieuw-Guinea." Bijdr. t. de T. L. en Vk. (2) 5. Amsterdam 1862, p. 140.

Zoology. — *"The value of generic and specific characters, tested by the wingmarkings of Sphingides"*. By Prof. J. F. van Bemmelen.

Supposing the rules for the colour-pattern of the wings, which I deduced from former investigations by others as well as by myself — to be valid, they ought to prove fit as guides in the choice of a point of issue, when entering on the investigation of a new group, that is to say when searching for a form which shows the general pattern in its most original, least altered condition.

Judging by those rules, I believe that among Sphingides, as far as I am acquainted with them, *Smerinthus populi* is a very original form, in spite of the covering of red hairs, spread over the upper side of the rootfield of the hind-wings, there hiding the primitive pattern.

The arguments for this opinion are the far-going similarity of fore- and hind-wing, both on the upper and the underside, and the presence of a pattern, which over the entire wing-surface is built after the same simple motive, viz. regular alternation of darker and lighter transversal lines and bands, each composed of spots. In both the dark and the light bands the spots show a strong tendency to the semilunar shape (the convex side turned outward), but here and there they clearly approach the biconcave (hourglass) form. As to the shades occurring as well in the dark as in the light bands of spots, I pass them over for the present.

On the upper side of the fore-wing two of the darker lines run on both sides of the light discoïdal spot, and at a certain distance from it, thus separating a darker median field from two lighter transversal bands, which in their turn are again bordered by a similar ribbonlike series of dark spots. Across this dark central area, at the outside of the light discoïdal mark, another dark bar may be distinguished, and in the distal part of the area, between the last mentioned bar and the outer borderline, there also occurs a series of spots, which however are far fainter.

Moreover the anterior edge of the wing, on the inner side of the discoïdal spot, shows a lighter hue than the rest of the central area, which increases in darkness toward the posterior margin. In this

lighter part two small dark spots touching the front-rim of the wing may again be distinguished, each of them composed of two transverse striae. In some specimens of *Smerinthus populi* the proximal border-rim of the central area is also clearly double. Next to the wing-root in the lightgrey hue of this part, a faint indication of a dark ribbon may be detected besides.

Of the various hitherto mentioned bars of dark spots, the outermost, which is by far the strongest and completest, consisting of nine separate elements when accurately counted, takes a sinuous course. Counting from the front backwards, the fifth spot is situated furthest inward, it also is the shortest and straightest. In many specimens this spot is obviously darker in hue than the rest, and this difference deserves our attention, as it is met again in allied species, but here increased in intensity and extension.

On the inner and on the outer side of the just mentioned rows of spots there occurs a broader bar of less obscure and more faintly circumscribed markings, which however are evidently darker than the grey shade of the lightest wing-areas, playing the rôle of ground-colour. The outer of these two collateral bars is separated from the median series by a narrow sharply traced light interval. From the internal bar it differs by lesser regularity, some of its components being broader than the rest, and at the same time darker. This is especially the case with the spot near the hindborder of the wing, this spot broadening obliquely in an outward and posterior direction, and thereby just touching the hinder angle of the wing. A similar triangular broadening also occurs at the front end of the bar, near the apex of the wing, but here it has a lighter hue. I think it desirable to indicate these spots by special names, e. g. anterior and posterior triangular spot, as they are found again with increased clearness and independence in allied species

In the middle part of the bar under discussion four of the spots clearly show the hourglass-type. In front of them the bar coalesces with a dark area, extending along the greater part of the outer margin of the fore-wing. This area forms a large convex blotch, occupying five internervural cells from the apex backward.

Though at first sight this blotch is not divided into separate spots, yet three darker centres may be distinguished in it, touching the foreside of the nervures which take their course through it. A comparison with other species of the same genus and of different allied genera again proves, that these darker centres may be considered as originally independent separate spots — one in each internervural cell—which have coalesced with each other into a single

almost homogeneous dark blotch. In front next to the apex, this blotch is sharply cut off from the above mentioned anterior triangular spot by an oblique light-hued line, the lastnamed spot moreover often showing a very light shade itself.

Now directing our attention especially to the points of correspondence between the various components of this wing-pattern, and on the contrary less heeding the differences, we are easily led to the conclusion that it is composed of seven transverse rows of dark spots, separated by lighter bars.

The external of these transverse rows (I) must then be looked for in the above-mentioned dark blotch along the external margin.

The second (II) is the complete row of nine spots, with its set of accompanying fainter bars.

The third (III) forms the external border of the dark central field.

The fourth (IV) is the dark line along the outer side of the discoidal mark, which although somewhat obliquely, may be said to run across the middle of the central area from fore- to hind-margin.

The fifth (V) is the inner front-line of the central field, this line being sometimes double.

The sixth (VI) the single, curved series of spots over the middle of the proximal light wing-area.

The seventh (VII) is formed by the faint traces of spots near the wing-root.

The light intervals between these seven bars may be indicated as in former publications by the letters A to G. In those intervals some traces of still other dark bars, varying in distinctness, are again met with; so it is not improbable that originally the stronger transverse bands everywhere alternated with less dark and sharply marked rows of spots.

In all these features the pattern of *populi* remarkably agrees with that of Arctiïds, as I described it in a former paper, and in the same way with that of numerous other families of Lepidoptera, as I hope to show afterwards [1]).

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[1]) Here I wish already to mention that ANNETTE F. BRAUN, in a paper: Evolution of the Color Pattern in the Microlepidopterous genus Lithocolletis (Journal of the Academy of Nat. Sc. of Philadelphia XV 2d Ser. 1914) as the result of an onto-genetic and phylogenetic investigation about the colour-development on the forewings of these Tineids, gives as her opinion that all patterns of this polymorphic genus may be derived from seven dark transverse bars, forming to her mind a primary pattern, on which a secondary one, composed of still darker lines, will later on be so to say projected, as is also proved by the development inside the pupal sheath.

Moreover this pattern occurs almost completely on the hind-wing as well as on the front one. For also there the first row forms a convex dark blotch occupying five internervural cells along the outer margin, with three darker centres next to corresponding veins. In the same way the transverse bar II is composed of dark spots, curved outward and is accompanied on both sides by a less dark bar of more diluted spots. The number of components of bar II is smaller than on the fore-wing, the hinder three being concealed under the covering of red hairs. The fourth and fifth spot (counting from the front border) are straighter than the rest, and placed somewhat more inward, while they show rather a darker hue.

Row III and IV stand in contact with the corresponding ones of the fore-wing, but disappear under the red covering even sooner than II. V and VI are only indicated by dark spots along the front margin, these spots moreover for the greater part being concealed under the overlapping fore-wing.

VII is totally invisible.

On the under side of the wings the pattern perfectly corresponds with that on the upper side, but on the fore-wing it is paler and partly indistinct, on the hind-wing on the contrary it is sharper and more complete than on the upper surface, because the red hairy covering is absent on the former. The front-rim of the hind-wing, remaining uncovered on this side, sharply contrasts both by colour and pattern with the rest of the wing-surface and wears one especially dark spot, forming the initial component of Bar IV. It seems desirable to indicate this peculiar spot by a special name, as it was also done with those of the fore-wing: viz. the hind-wing-frontborder-spot. In a single of the specimens at my disposal I also found the markings along the front-border of the under side of the fore-wing differentiated and specially spotted.

On the under side of the hind-wing Bar V and VI are not represented, either by their initial (frontal) elements or by other spots of their row, neither can Bar VII be distinguished; the light discoïdal marking however being well visible, as it strongly stands out against the broad anterior part of Bar IV.

Now let us compare this pattern of the Poplar Hawkmoth with that of the Eyed Hawkmoth. The close kinship of *Sm. ocellata* with *populi* appears from several points of correspondence, but surely most convincingly from the possibility of crossing these two species together, the reciprocal hybridisation leading to different results and the hybrids themselves being again fit for propagation. On these accounts the classing of these two species into two different

genera, as proposed by recent systematists, in my opinion does not give a true representation of these relations, but is only a consequence of the immoderate tendency to splitting up, which nowadays is so prevailing in systematic zoology.

To me the comparison between the wing-markings of these two species, so different at first sight, seems highly interesting, especially if the numerous byforms, which are described partly as independent species, partly as subspecies, races, varieties, aberrations etc., are also taken into account. Attention should also be given to the results of hybridisation. But in the first place the under side of the wings should be considered just as accurately as the upper one, and moreover fore- and hind-wing, on both their surfaces, should be compared to each other in detail.

If we do so with *ocellata*, it is easy to see that this species forms one of the innumerable proofs for the assertion, that the difference between fore- and hind-wing, upper and under side, is a consequence of secondary modification of a general primitive pattern, this pattern as a rule remaining better preserved on the under side than on the opposed surface, though as to the latter, the fore-wing usually has retained clearer and more complete vestiges of the primitive pattern than the hind-wing.

Starting with the upper side of this latter, the conviction is easily reached, that the eye-spot, in all its conspicuousness, is yet nothing else but a peculiar modification of parts of three parallel dark bars, each forming the termination of a transverse ribbon (parallel to the wing-border), these ribbons again resulting from the coalescence of a series of internervural spots [1]). Most convincing for this supposition is the comparison of *ocellata* with the nearly related species *Sm. coecus* and *kindermanni*, but it is already rendered highly probable by the comparative inspection of upper and under side of the hind-wing of *ocellata* itself. Such an inspection shows, that on the under side the three ribbons in question are continuous without interruption from behind unto the front border, the outmost one causing near to the hinder angle, where the wing-edge forms an incurvation, a marginal obscuration, which can be retraced on the upper side in the peculiar curved little stem, connecting the eye-spot with the hind border.

On the under side therefore no indication of an eye-spot is present, the dark bars running from before backward without interruption

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[1]) This proof has been ably and convincingly delivered by Dr. J. Botke, in his paper: Les motifs primitifs du dessein sur les ailes des Lépidoptères et leur signification phylogénétique. Tijdschr. der Nederl. Dierk. Vereeniging XIV, 1916.

or modification, separated from each other by two narrow, very light intervals.

Along the outer side as well as toward the wing-root these three bars are accompanied by rows of dark spots. The row at the marginal side represents the big semilunar blotch, which occurs on this same place in other species of Smerinthus, and forms the homologue of the corresponding patch at the outer margin of the fore-wing, which occurs in *ocellata* as well as in numerous other species. We here find the convincing proof that this dark marginal area is formed by the coalescence of a row of spots. The middle row of the three ribbons of dark spots is evidently double, its members forming a series of square blocks, whose inner and outer side are formed by dark strokes, sometimes straight, in other cases slightly curved. The outer of these border-strokes are the darkest. The comparison with *populi* proves that these dark strokes represent bar II. As in *populi*, this bar is therefore accompanied at both sides by a dark seam. The one on the outer side is much broader, darker and more independent than the seam on the inner side. The latter is separated from Row III by the inner white band, this row only forming a narrow line, connected by a dark interspace with the very dark and complete Bar IV, which runs along the outer side of the light discoïdal marking, in the same way as in *populi*.

On the under side of the fore-wing the same spots and bars can be found, with the exception of Bar IV, which remains entirely concealed under the wine-red hairy covering of the root-field, just like the posterior part of Bar III. It is only the discoïdal marking, which maintains itself as a small whitish patch in the middle of this reddish covering.

But also on the upper surface of the hind-wing traces of these same bars may be noticed, viz. along the front border, on that part of the wing that remains hidden under the fore-wing during flight, but is protruded in front of it during rest, in consequence of the peculiar attitude of fore- and hind-wing in regard to each other. On this part three dark double-lines run backward up to near the beginning of the red hue, and there end blindly. To my view there is no reasonable ground for the supposition, that these vestiges of pattern should have secondarily crossed over from the fore-wing to the freely protruding part of the hind-wing. On the contrary it seems justified to assume, that they belong to the primary pattern of the hind-wing, as well as their homologues on the under side, or those on the upper side of the hind-wing of *populi*, and have remained untouched by the red discoloration.

Returning to the upper side of the fore-wing, it is at once clear that the same pattern occurs on it as on the corresponding wing of *populi*. It is only somewhat more differentiated: the dark middle area is broken up into a fore- and a hind-part by a narrow funnel-like slit of light colour, along the course of the second cubital vein, while the middle-member of the dark Ribbon II has increased in bulk and shade to a very dark square.

In the same way the anterior and posterior triangular spot, especially the latter, are much more conspicuous and independent than in *populi*.

By proceeding this way we can gradually arrive at the probable conclusion that the patterns on upper and under side of both fore- and hind-wing of *ocellata* repose on one and the same groundplan, and that this primitive pattern has suffered the strongest modification on the upper side of the hind-wing, in consequence of its partial overshadowing by a red discoloration and of the differentiation of the back part of the pattern to an eye-spot.

Should further proof be needed, that the pattern of *ocellata* takes its issue from the same groundplan as that of *populi*, this proof, as already remarked, would be furnished by intermediate forms as *coecus* and *kindermanni*.

As far as the markings on the upper side of the fore-wing, *Sm. coecus* corresponds more to *populi* than to *ocellata*, the transverse bars being more complete and more purely traced than in the latter. Especially the dark middle area is not split up into a fore- and a back-part, the Bars III, IV and V therefore all running straight and unbroken from before backward, V in particular being sharp and dark.

On the hind-wing the eye-spot is less purely circular, because the external (hinder) dark line and the black pupilla-line are less rounded and more advanced toward the hind-margin, thereby giving the impression of fragments of ribbons.

On the other hand the vestiges of original design along the front-margin, hidden under the hind-rim of the fore-wing, are less conspicuous than in *ocellata*.

On the fore-wing of *kindermanni* (Fig. 3) the median area is broken up as in *ocellata*, and in general the similarity with the last named species is greater, the design appearing only somewhat sharper, especially Bar VII looking thereby more conspicuous. The convex blotch along the outer margin is divided into a smaller anterior and a bigger posterior part. The pink hue on the hind-wing is particularly vivid in tone, but the eye-spot is perfectly flat and

composed of three almost similar pieces of dark ribbons, so that its eye-character is almost gone [1]).

On the under side the similarity with *ocellata* is very striking.

By the consideration of the colour-pattern of *ocellata*, as well in itself as in comparison to that of *populi*, we therefore come to the following general statement:

In contrast to *populi*, the pattern on the upper side of *ocellata* deviates from that on the under side, and is moreover composed of two heterogeneous parts, a far-going difference existing between that of fore- and hind-wing. Yet it proves possible to deduce the pattern of both wings from the design of *populi*, which in this latter is especially developed on the upper side, but which can be retraced, be it in a fainter and more reduced condition, on the inferior surface.

The pattern of *populi* therefore satisfies the general conditions of a primitive design, that of *ocellata* those of a secondarily modified, viz.: dissimilarity between the upper side of the fore- and the hind-wing, as well as between the upper and the under side of both wing-pairs, in consequence of deviations of the upper side (of fore- as well as of hind-wings) from the original, simple and regular pattern, but this in a different sense for the two wings, the hind-wing deviating more widely than the fore one. On the first-named a tendency to annihilation of large parts of the pattern by the influence of selfcolour prevails, combined with an extraordinary differentiation of the remaining fragments, this leading to great contrasts between the areas (eye-spot on pink ground). The fore-wing on the other hand shows the complete original design, but transformed over all its components in a more or less similar manner: some parts thereby prevailing above the rest, without affecting however the general harmonious character of the whole.

These facts might easily lead to the conclusion, that the peculiarities in the design of the upper side, by which *ocellata* differs from

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[1]) In parenthesis it may be observed, that we therefore are able to prove for the eye-spot on the wings of the imago a similar origin as A. WEISSMANN so ably did for those on the body-rings of the larvae of Sphingides, viz. that they spring from fragments of a set of longitudinal, alternately light and dark stripes, these fragments becoming independent and differentiated to concentric circles, while the rest of the stripes disappears totally or nearly so. In caterpillars these stripes run parallel to the body-axis, on the wings of the imagines they are seemingly transverse. Considering wings to be folds of the body-skin, it is easy to conceive, that these so called transverse stripes in reality correspond to longitudinal stripes on the insects' body. Probably the latter stripes may as well as those on the wings be considered as rows of spots which have coalesced together.

populi, should be considered as specific features of the first-named form, whereas the points in which the two species resemble each other, especially on the under side, would possess the significance of generic characters. This opinion, that e.g. the eye-spot of *ocellata* cannot pretend to a higher significance than that of being a specific peculiarity, might not only find support in its restriction to the upper side, but also in the results of hybridisation, showing that the hybrids from the cross between a male *ocellata* and a female *populi* are *ocellata*-like in their habitus, though with a faint eye-spot, deprived of its pupilla, whereas those from the combination of a male *populi* with a female *ocellata* possess such a far-going similarity to *populi*, that they can hardly be distinguished from it, the eye-spot being wholly absent.

This view about the meaning of the differential features of *ocellata* seems the more attractive because a special importance for the chances of survival of the animal may be ascribed both to the variegated and marmorated design of the fore-wings and to the eye-spots, in their monochrome pink field, of the hind ones. As long as the moth in its attitude of rest is suspended on a willow-twig among the leaves of that food-plant of its caterpillar, the hind-wings are concealed under the fore-wings with the exception of their narrow fore-rim, and the animal so delusively imitates by its form, colour, design and proportions of a pair of dry willow leaves, that notwithstanding its bulky size it can hardly be detected amongst its natural surroundings, as long as it remains motionless.

When however the sleeping moth gets disturbed by pushing or hurting, it moves its fore-wings a little forward, thereby suddenly displaying the eye-spots in their red surroundings, which by their situation on both sides of the somewhat upheaved abdomen (this part of the body at the same time making periodical jerks) cause the illusion of a savage face with wide-opened eyes, thereby (as experiments have proved) so effectually frightening birds and reptiles, that they generally abstain from further attempts to devour the moth.

When I mention these long known facts from the chapter of Protective Mimicry, it is because I think it desirable to state once more, that they can never be used as an explanation of the presence of markings, hues and shapes, which by their coöperation call forth the deceitful resemblance. These features owe their presence to causes of quite another order of things, viz. to the variability, which itself is a consequence of the coincidence of hereditary factors. When this coincidence accidentally leads to an effect which in a certain direction is favourable for chances of survival of the animal (or plant), it

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will always be preserved and ameliorated by the influence of natural selection, so that it will give rise to those highly finished cases of mimicry and protective resemblance which so often raise our astonishment and admiration.

One of the reasons that have made it seem desirable to repeat once more these opinions, however often proclaimed before, is the fact that DE MEYERE in his recent paper "Zur Evolution der Zeichnung bei den Holometabolen Insekten", when arguing on page 59 against BOTKE's views about the wing-pattern of Cossids, declares that he can only see in their design "eine hochgradige Entwicklung einer sympatischen borkenähnlichen Färbung", while on page 48 of his preceding article "Zur Zeichnung des Insekten-, im besonderen des Dipteren- und Lepidopterenflügels", he derives this design "aus einer Zeuzera-pirina-ähnlichen Fleckenzeichnung". To this he adds: "Dieser Weg scheint mir besser verständlich als der umgekehrte". And somewhat further on he says about the transverse markings on the under side of several Vanessidae: "diese scheinen mir mit dem primären Zeichnungsmuster überhaupt nichts zu tun zu haben, sondern es sind eher spät erworbene Elemente der sympathischen Färbung".

The point in these considerations of DE MEYERE which I want to discuss, is not his opposition against BOTKE's views about the connection between spots, stripes and nets, to which I cannot pay full adhesion either, but his assertion, that by considering a wing-design as a "sympathetic pattern" an argument is raised for the explanation of the origin and the discovery of the age of this pattern. Patterns of all kinds, the most original as well as the most strongly modified, may produce a mimicking effect, and thereby prove useful for protective purposes.

E.g. the wing-design of *populi* has quite as much protective value as that of *ocellata*, though only in the sense of resemblance to a weathered poplar-leaf, and yet it is much more primitive than the latter. Moreover the same motives and elements of design, which in one species of animal are the source of highly imitative mimicry, may also be found in other species, near akin as well as far removed in a generic sense, but here, by showing a somewhat different form or by occurring in another part of the body, only cause a feeble sympathetic resemblance or no mimicking effect at all. Of this so called false mimicry EIMER has cited several instances.

Numerous thin, irregular transverse stripes between the veins, in the sense of BOTKE's "traits effilochés", are found except in Vanessidae in many other Lepidoptera of diverse families: also in Sphingides,

on both wing-sides, though most frequently on the under side. In a general survey of the wing-markings of Lepidoptera, which I undertook long before Botke's doctor-dissertation, and wrote in English, but which I did not hitherto publish, I even thought it desirable to choose a special name for this curious motive of design and called it "Cosside markings".

Now it might very well be, that these markings could also be reduced to an old and original motive of design, occurring generally among insects, and whose connection with the system of internervural spots still wants elucidating, although Botke has made a notable attempt to come to a general theory.

That a "sympathetic" design, on account of its mimetic character, should necessarily be younger than other patterns, I deny most emphatically. Each of the elements, which by their coöperation produce the mimetic effect, may in itself depend on hereditary tendencies of very high phylogenetic antiquity. Only the specific and special culmination of that coöperation may be young, and even this need not necessarily be the case. Among Pierids, Papilionids and Nymphalids the mimicrists probably often wear an older and more primitive uniform than the remaining so-called typical members of these families, as I have tried to demonstrate in my paper read at the International Entomological Congress at Oxford in 1912.

In numerous Geometrids, issuing from their pupae in autumn, the similarity to a weathered leaf reposes on their light-yellow colour, besides on the broken rim of their wings and the course and arrangement of dark transverse lines on them, imitating the veins of the leaf. Must on this ground the yellow hue be younger than other tints? According to my view this need no more be the case than it need be assumed for the form of the wing-border or the pattern on its surface, even when granting that in general a broken border-line has to be derived from an unbroken, rounded one.

In the same way the evident connection between spots, stripes and meshes on the wings of Cossids, which can so to say be read on the wing-surface by simple observation and by comparison with the Zeuzerids, is in no way brought nearer to an explanation by the remark, that the preponderance of the net-markings produces a sympathetic resemblance to the bark of trees. The real question remains: what causes tendency of the Cossid wing-markings to the net-character and how old is that tendency? In putting this question we have to keep in view, that the same tendency occurs in many other insects

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belonging to different orders and that it may likewise be remarked in the nervural system, which possesses such intimate and primordial relations to the distribution of pigments in the skin.

Were it only to consider this question from all possible points of view, the well-foundedness of the hypothesis would have to be tried, whether net-design may be connected with the formation of meshes in the system of wing-nervures, as is so frequently and specifically found in Neuroptera and Orthoptera, vicariating with regular transverse venation; whether therefore the net-design may not be as old as or even older than spots or stripes. An argument to this assertion might be found in the fact, that nets between the longitudinal veins are characteristic of the nervation of the wings in Palaeozoïc Palaeodictyoptera.

With this inference I do not in the least intend to proclaim, that I am convinced of this connection of the net-design and of its phylogenetic antiquity, but simply that I think the contrary is not proved either.

Remembering WEISMANN's words: "Ohne Hypothese und Theorie giebt es keine Naturforschung", I am of opinion that the continual proposing of explaining suppositions about the connection between corresponding phenomena is necessary condition for fertile scientific research, and therefore I cannot adhere to DE MEYERE's point of view, where he says: "Ich möchte mich, den Tatsachen entsprechend, mit Feststellung des Auftretens begnügen und keine ganz hypothetische Verbindungslinien ziehen."

Returning to the specific differential characters of *Sm. ocellata*, I here find the danger to get entangled in purely hypothetical speculations not by any means serious. For it can be easily proved that all the special characteristics of the upper side of both fore- and hind-wings occur as well in other species, not only of the genus Smerinthus, but also of different allied genera.

In the first place the comparison with *tiliae* is highly instructive. On the upper side of the fore-wing of the Limetree-Hawkmoth every peculiarity by which the pattern of *ocellata* deviates from that of *populi*, is again met with, but in a modified form and in other hues, which together produce a totally different effect of the wing-design as a whole.

Especially striking is the similarity of the dark median area with the same wing-part of *ocellata*; as in the latter it is cut up into a fore- and a hind-quarter by funnel-shaped intrudings of the light-brown ground colour, which may either meet each other or remain separate. A single look at every somewhat considerable collection

of *tiliae* shows the extreme individual variability of this feature, as well as of others. The transition of an unbroken middle-field to one divided into an anterior and a posterior portion we therefore here see take place under our eyes.

We may likewise notice, that the peculiarity of the central (5th) mark of the dark Bandline II, to differ in hue and size from the other members of that series, is also present in *tiliae*, but in so far in an opposed sense, that in some specimens it is distinguished by a lighter instead of a darker shade. On its underside, *tiliae* shows again the same simplified pattern as *populi* and *ocellata*, viz. the two Bandlines II and III, with traces of I, IV and VI.

The right here to speak of simplification, and to connect this with the covering of light hairs stretching from the wing-root outward as far as the middle area, is strikingly proved in this case by the vestiges of the opaque central blotch (so strongly developed on the upper side) which can also be detected on the under side. At the root of each hair in the area of this dark middle-field a small black speck may be perceived, and this produces the effect that the field is seen in its full extension as a collection of specks, when we look obliquely between the hairs.

Still more striking than the resemblance between *tiliae* and *ocellata* is that between both these species and *tartarinovii*, this latter offering so to say a form of transition between the first-named two. Here the anterior part of the external margin of the opaque middle area is not convex as in *tiliae*, but is concave, while a contrast both in hue and in markings exists between the anal field of the wing and the rest of its surface, the division of the central field in a fore- and a hind-part thereby appearing as part of a process which extends over the whole length of the wing-surface, in the same way as in so many other Lepidoptera and even in Insects of other orders.

It is likewise remarkable, that the apex of the fore-wing, which shows a special differentiation identical for all these species, viz. that it is separated from the remaining markings by the oblique light stria already described for *populi*, is dark greenish grey instead of silvery grey, in contrast with the convex blotch along the outer margin, which is stained in light grey, while it is dark in others.

On the hind-wing *tartarinovii* displays the same pink as *ocellata*, and even traces of an eye-spot.

On the other hand in *tiliae* a dark band extends over the entire surface of the hind-wing parallel to the outer margin and at some distance from it. This band evidently consists of as many components

as there are internervural cells. Each component is prolonged wedge-like in the direction of the wing-root. The extent of this prolongation is individually different, though in general it may be stated, that in a backward direction toward the hinder wing-edge the dark internervural spots get larger and more intensively black, this backward increase in size and darkness being the only indication of a similarity to the eye-spot of *ocellata*.

Therefore, though in this latter instance *tiliae* shows almost as little likeness to *ocellata* as does *populi*, this does not derogate from the truth and the value of the fact, that in numerous Sphingides the hinder external angle of fore- as well as of hind-wing shows a dark pigmentation, which may be differentiated to an eye-spot. This might also be expressed otherwise, by saying that the above-mentioned posterior triangular spot is not restricted to the fore-wing, but returns on the hind-wing.

And also on the fore-wing the spot in question may assume the character of an eye-spot, as is shown by several Sphingides belonging to different genera, e.g. *Daphnusa ailantha*.

On the other hand, as already said, other species possess near to this hinder external angle of the fore-wing only a single or double, solid blotch not differentiated to an eye-spot, e.g. *Oxyambulyx canescens*. Also this blotch may be repeated on the hind-wing, e.g. *Smerinthus quercus*.

Among the Sphingides at my disposal *Pholas labrusiae* (Fig. 6) seems to me to possess a highly remarkable colour-pattern. On its under side the similarity between fore- and hind-wing is very great, and both show the usual simple design of Lines II and III on a nearly homogeneous faint greenish-yellow ground, to which only along the external margin a differently coloured area, separated from the rest of the wing-field by a zigzag line, and evidently representing Bar I, is added. But on the upper surface the contrast between the two wing-pairs is very profound. The fore-wings are almost unicolourous dark opaque green, exactly corresponding in hue to the entire body of the moth. Yet several traces of dark transverse lines are well defined, especially the middle-field between Bars III and IV, which is conspicuous by a somewhat darker green shade. But at the external border of this middle-field two square little areas are so to say spared out from the general green overshading: one nearly in the centre, the other at the back margin, thereby giving the impression of brown curtains before two low windows in a green wall. That impression is strengthened by the fact, that in these brown areas the curved components of the transverse dark bars are more numerous

and far sharper than in the green field. In the central window 4 of these arched stripes are present, in the back one 2.

Comparison with *Smerinthus populi* and *ocellata* as well as so many other Sphingides, whose ground-colour is brown or grey, and whose transverse bands are composed of curved, stripy spots, leads to the supposition that in these windows we have to see remnants of the original hue and design of the wing, which for the rest has become indistinct by green discoloration.

As in so many other cases, e. g. the Hepialids, green therefore would be the secondary, brown the primary hue, the design having partly get lost in the process of discoloration or at least having greatly diminished in distinctness. But why these two brown windows with their trelliswork of curved stripy spots have remained untouched by this process, I cannot as yet explain.

Contrasting with the almost homogeneous green hue of the fore-wing, the hind one possesses a very showy and variegated pattern: two jetblack bars standing out against a light yellow ground, bluish-grey areas occurring at the front border between the black, a brickred patch vicariating with two black strokes near the inner margin, while at the outer one a small green field breaks the yellow.

But the most remarkable point in this pattern are two darkbrown, irregular, denticulate lines, starting at the hinder angle, and running parallel to the outer margin along its posterior part, to pass into the broad black bar at the hinder border of the small green field. These crooked lines represent the posterior part and the pupilla of the eye-spot in the *ocellata*-group among Smerinthidae, and form the least-modified part of the hind-wing-pattern of *Pholus labrusiae*. I think it highly probable, that this pattern has a protective significance for the animal, just as well as the almost homogeneous green hue of the fore-wings and of the body. The latter give protection to the sleeping animal by making it hardly visible to enemies that prey upon it, possibly the brown windows play their part in this process of concealment, by breaking the anatomical lines of the rather extensive wingfield.

It certainly would be worth while to make the experiment, whether the moth when disturbed in its sleep, suddenly displays its hind-wings and so frightens its enemies away, or whether the showy colour-composition, which thereby gets visible, has only the meaning of a warning-pattern, announcing unpalatableness.

Whatever may be the right interpretation, this pattern in any case ought to be considered as a high and special differentiation of the original one of the hind-wings, common to all Sphingides; neither

the crying colours nor their queer arrangement justifying the inference that they could ever be the direct consequences of the useful effect they produce in favour of the animal.

The comparison of *Sm. ocellata* with *populi*, and of both with other Sphingides, leads me to the following conclusions:

The colour-pattern of *populi* is more primitive than that of *ocellata*, it agrees with the conditions which may be posed for a primordial pattern, and it corresponds to the fundamental plan, as this is found in Arctiïds, and most probably in numerous other families of Heterocera, possibly also in Rhopalocera. It therefore is not only older than the genus Smerinthus, but even than the family of Sphingides, perhaps than the entire order of Lepidoptera. So it cannot without great restriction be qualified as a generic pattern.

The colour-design on the upper side of *ocellata* can be derived from that of *populi* by the assumption, that the ribbons of internervural spots occurring in the latter have been specially transformed in the former. But each of these transformations in itself is seen as well in other species of Smerinthus, and even in many other genera of Sphingides, it is therefore not allowable to assume, that they should have been acquired during the formation of *ocellata* from a *populi*-like ancestor. Each for itself they are not characteristic of *ocellata*, and cannot be taken as specific features of this species. It is only the peculiar combination of the modifications of the ancestral type with the subtle nuances by which in *ocellata* they are distinguished from the similar modifications in allied forms, that in the end give the specific character to *ocellata*. At any rate the origin of the said modifications of the primitive pattern cannot be ascribed to the influence of protection against enemies, which *ocellata* obtains by the use she (instinctively) makes of her eye-spots. The special refinement however and the elaborate details, by which the pattern of *ocellata* surpasses that of other Sphingides near akin, may well be the consequence of natural selection, which could enter into action as soon as by coïncidence of hereditary variations of the fundamental Sphingidial pattern with special circumstances of life, a deceitful likeness had been established to the face of a big-eyed owl, which frightened away preying little birds and small mammals.

Groningen, October 1918.
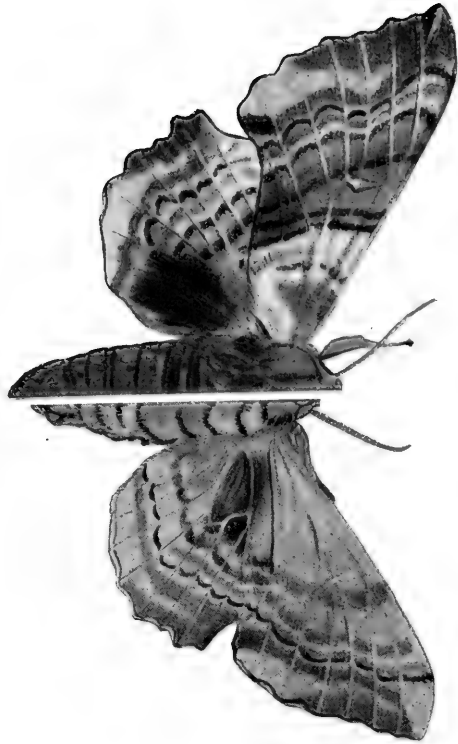
1. POPULI

2. OCELLATA

5. TARTARINOVII

4. TILIAE

E. THEYSSEN, Phot

3 KINDERMANNI

2 OCELLATA

1 POPULI

6 LABRUSIAE
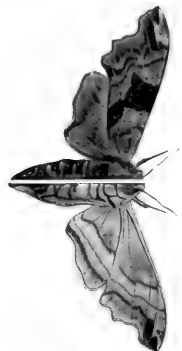
5 TARTARINOVII

4 TILIAE

Anatomy. — *"On Musculus Transversus Orbitae"*. By Dr. A. A. Hueber. (Communicated by Prof. J. Boeke).

(Communicated in the meeting of November 30, 1918).

This muscle variety, already described by Bochdalek [1]) was seen in the body of a woman of 33 years of age. In many respects it is different from Bochdalek's finding; it may, therefore, not be undesirable to publish this case. The muscular anomaly was present in either orbit; the right- and the left-musc. transversus displayed some points of difference.

In the *left orbit* (Fig. 3) the musc. transversus generally passes right across the equator of the eyeball, and is inserted into the inner as well as into the outer wall of the orbit.

About two mm. behind the trochlea the muscle arises from the anterior part of the lamina papyracea ossis ethmoïdalis, to which it is attached by a broad, thin, flat tendon about 7 mm. in width.

The tendinous fibres soon become muscle fibres; the muscle, now proceeding laterally, gets narrower and more rounded and passes as a small muscle, 2 mm. in breadth, below the musc. obliquus sup., decussating the latter at right angles. At a distance of about 1 cm. from the medial orbital wall the muscle widens and flattens coincidently. This widening is brought about by the fact that muscle fibres, issuing from the medial margin of the musc. levator palpebrae sup., bend round towards the medial, and pass into the musc. transversus. The musc. transversus then proceeds farther laterally and is seen to decussate the fibres of the musc. levator palpebrae in a very peculiar way. The fibres of the musc. transversus pierce those of the musc. levator palpebrae, but in such a way that the musc. levator runs for the greater part across the upper side of the musc. transversus; only a small muscular fascicle of about 3 mm. across, passes below the musc. transversus.

The two parts of the musc. levator, separated by the musc. transversus, unite again when coursing anteriorly. At the point of decussation the musc. transversus has a breadth of ± 4 mm., the musc. levator of about 10 mm.

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[1]) Bochdalek, Beitrag zu den anomalen Muskeln in der Augenhöhle. Vierteljahrschrift für die Praktische Heilkunde. Prag. 1868. Bd. IV.

Laterally from the point of decussation the musc. transversus passes into a thin flat tendon that goes below the gland. lacrimalis to the lateral orbital wall, and is inserted below the inferior edge of the lachrymal gland into the lateral orbital wall.

After the decussation the musc. levator palpebrae splits in the usual way into an upper- and a lower-sheet. The upper one soon expands into a tendon, which is attached to the skin of the upper eyelid, medially to the tartus sup. and to TENON's capsule, and laterally to the anterior part of the lateral orbital wall. The relations of the lower sheet are somewhat anomalous. After the splitting up of the upper sheet, the lower one passes into a strongly developed sheet of smooth muscular tissue: the musc. tarsalis sup. The lateral free border of the lower sheet has a length of about 3 mm. and then blends with TENON's capsule. The lower sheet now stretches in the normal way towards the anterior and settles at the upper mar- gin of the tarsus sup.; the medial part of the sheet has the same insertion points as the upper sheet, for on this side the two sheets are united. The lateral part however is more expanded than usual.

According to VIRCHOW [1]) the two lateral borders of the upper and the lower sheet lie over each other; in our preparation this is not the case, for we see that the lateral part of the lower sheet stretches more backwards. Now this part of the lower sheet unites with the lateral expansion of the musc. transversus and thus the two constitute a tendinous sheet, gliding below the lachrymal gland to the lateral orbital wall and is inserted into it as a broad flat tendon, 20 mm. across. This tendinous sheet is grown together with TENON's capsule as was observed above to be the case also with the lower sheet of the musc. levator palpebrae. The orbital part of the lachrymal gland is found for the greater part on the tendinous sheet formed by the musc. transversus and the musc. levator palpebrae; a small portion of it overlaps anteriorly the lateral border of the upper sheet of the musc. levator. The conjunctival part of the lachrymal gland is located between the two sheets of the musc. levator palpebrae.

In the *right orbita* [2]) (Fig. 2) the aspect of the musc. transversus is on the whole the same as in the left; in the former, however, the muscle is more developed than the left. It also arises from the anterior part of the lamina papyracea ossis ethmoidalis as a

[1]) H. VIRCHOW, Über TENON'schen Raum und TENON'sche Kapsel. Abhandl. der Kön. Preuss. Akad. der Wissenschaften. 1902.

[2]) In the right orbita the musc levator palpebrae is cut through, the better to show the course of the musc. transversus.

strong tendon of approximately 8 mm. across, and is seen to lie against and somewhat below the trochlea. After the flat tendon, long about 3 or 4 mm. has changed into muscle fibres, the muscle here also gets narrower, and when it follows its way below the musc. obliquus sup. has a breadth of 3 mm. and a thickness of 1 mm. At a distance of 7 mm. from the medial orbital wall, the muscle widens again, as also happened on the left side, because fibres, coming from the medial border of the musc. levator palpebrae bend medially and pass into the musc. transversus. Subsequently the muscle decussates the musc. levator palpebrae at right angles and glides almost entirely below the musc. levator. Only two narrow muscular bundles of the musc. levator, each about 1 mm. across (a Fig. 1) follow their way through resp. below the musc. transversus, and after proceeding anteriorly, join the bulk of the musc. levator. At the point of decussation the breadth of the musc. transversus is 6 mm.; that of the musc. levator 14 mm. Then the musc. transversus extends further to the lateral orbital wall, glides below the gland-lacrimalis and attaches itself in the same way as on the left side to the lateral orbital wall.

The union of the musc. transversus with the lower sheet of the musc. levator palpebrae accords completely with that of the left side. The musc. tarsalis sup. is still more strongly developed here
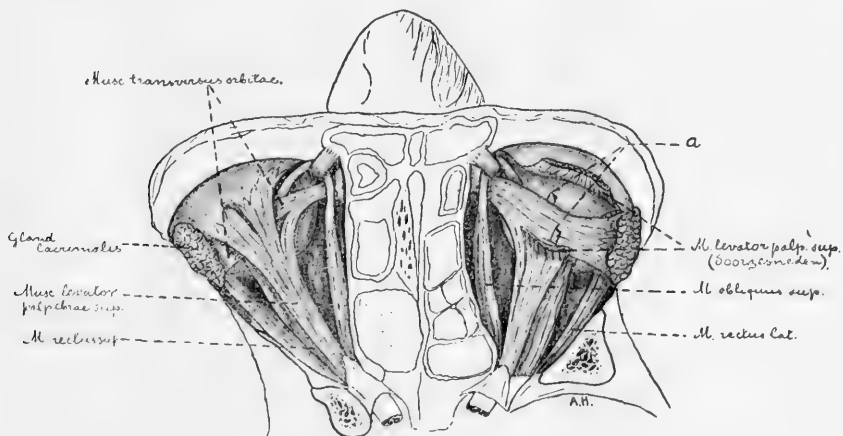
Fig. 1.

than the left one, above all laterally. The free border of the lower sheet of the musc. levator palpebrae is here ± 5 mm. in length; the lower sheet then unites with the lateral extension of the musc. transversus, and both form as on the left side a tendinous sheet, attached to the lateral orbital wall with a breadth of 18 mm. Here

also the tendinous sheet is blended with TENON's capsule. The relations of the lachrymal gland are similar to those on the left side.
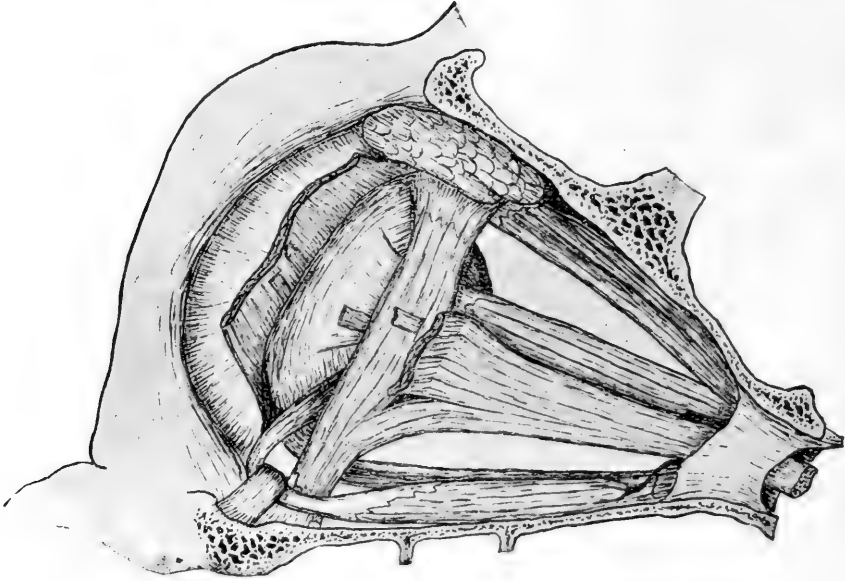
Fig. 2.
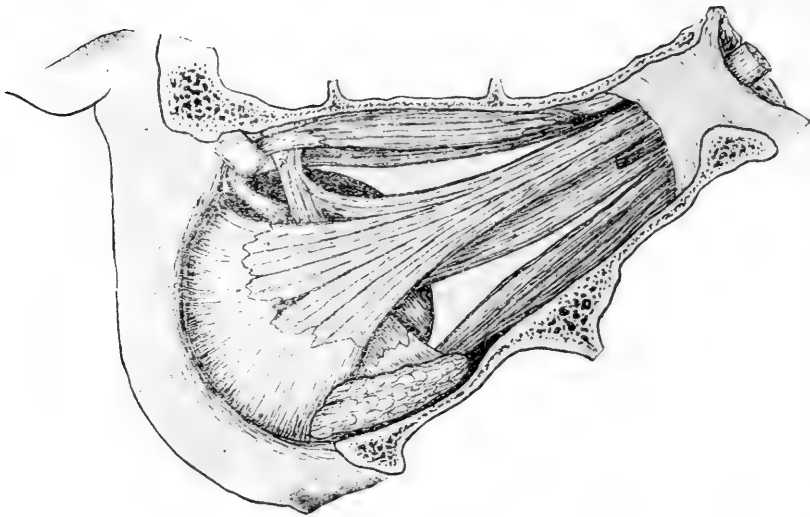
Fig. 3.

It appears then that the principal points of difference between the right and the left musc. transversus are that the right musc. transversus is more strongly developed than the left one and that the right musc. transversus extends further beneath the musc. levator palpebrae than the left one.

Now when comparing the case discussed just now with Bochdalek's finding, remarkable differences come to the front.

Bochdalek saw the musc. transversus continuous with the musc. gracillimus, which has been described before by Albinus [1]), and was closely related to the musc. transversus. The said musc. gracillimus is absent in our case, which, therefore. is the first case in which the musc. transversus occurs uncomplicated with other abnormal muscles.

Furthermore Bochdalek calls attention to the fact that a close relationship existed between the musc. transversus found by him and the musc.-levator palpebrae, in such a sense that most fibres of the two muscles were blended inseparably, and that others bend round partly anteriorly, partly posteriorly, towards the medial border of the musc. levator palpebrae, while blending with the latter; while a considerable part of the musc. transversus pierced through the musc. levator and ran to the lateral orbital wall. Now when drawing a parallel between this description and ours, it is evident that a close connection between the musc. transversus and the musc. levator palpebrae is entirely out of the question here.

First of all there is in our case no bending forward of fibres of the musc. transversus. Secondly we do not note an inseparable blending of the fibres of the musc. transversus and the musc. levator palpebrae. Thirdly in our case there is, strictly speaking, no piercing of the musc. levator palpebrae by the musc. transversus, because the musc. transversus runs almost entirely below the musc. levator palpebrae and only few slender muscle fascicles of the musc. levator pass below the musc. transversus, and that only in part.

The principal points of agreement are the connection with the lower sheet of the musc. levator palpebrae and with Tenon's capsule, and the relation to the lachrymal gland.

As regards the innervation of the musc. transversus, we are sorry to say nothing can be recorded. When the muscle was found, the upper fat-layer together with the nerves had on both sides got lost in the preparation. Bochdalek only reports an innervation of his left musc. transversus by very tiny branches of the nn. frontalis and lacrimalis.

The function of the musc. transversus orbitae is naturally difficult to ascertain. Bochdalek considered the musc. transversus to be a complex musc. transversus internus and externus. When co-operating from the two insertion points (internal and external orbital wall),

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1) B. S. Albinus, Historia Musculorum Hominis. Lugd. Bat. 1734. p. 176.

they would maintain the musc. levator palpebrae in position, and thereby sustain its leverage. Each part would of itself be capable of dragging the musc. levator palpebrea more or less to its own side, and thus drag the medial part of the eye-lid up- and inwards, resp. the lateral part up- and outwards.

The connection to TENON's capsule would render an action on it possible and consequently assist in the leverage of the musc. levator palpebrae. Lastly, in consequence of the strain of the whole musc. transversus, the broad, lateral tendinous expansion would perhaps press the lachrymal gland tighter against the superior orbital wall and compress it more.

MACALISTER [1]) believed that the musc. transversus was a displaced, deep slip of the pars palpebralis of the musc. orbicularis oculi. However, in my judgment the connection between the musc. transversus and the musc. levator palpebrae is too close for me to share his view.

If MACALISTER's view were correct, it would follow that the fibres would extend beyond the musc. levator palpebrae. But, as noted before, in our case, and in BOCHDALEK's case also, not a single muscular fibre of the musc. transversus runs beyond the musc. levator palpebrae; in our case the transversus-fibres pass chiefly beneath the musc. levator. This experience is supported by MACALISTER's finding that he saw deep slips of the musc. orbicularis oculi coursing in about the same place where we found the musc. transversus, and that these fibres ever occurred outside the musc. levator palpebrae.

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[1]) A. MACALISTER. A Descriptive Catalogue of Muscular Anomalies in Human Anatomy. Transact. of the Roy. Ir. Acad. Vol. XXV. Sc. Dublin 1872.

Zoology. — *"On the Anatomy of the Larva of Amphioxus lanceolatus and the Explanation of its Asymmetry"*. By Prof. J. W. VAN WIJHE.

For many years I have attempted to complete a part of the many lacunae in our knowledge of the morphology of Amphioxus, because this morphology is in many respects the basis for the comparative anatomy and embryology of the Vertebrates.

After the publication in 1914 in the Transactions of this Academy of my work on the changes of the larva of Amphioxus during the metamorphosis, during which growth ceases, I have managed to obtain sufficient material to investigate the larva during the growth-period. Now that the research and the necessary drawings have been completed — the text must still be written — I shall here discuss some results.

Many years ago (1893) I found that the mouth of Amphioxus was only apparently placed more or less symmetrically, that in fact however it lies exclusively on the left side as the nerves and muscles of the buccal cavity without exception belong to the left side of the body, which was later on confirmed by others. This fact is in accordance with the earlier discovery of KOWALEVSKY (1867) that the buccal opening in the larva of Amphioxus is situated, not mesially, but on the left side of the fore-end of the body.

Through its mouth, which is a mesial organ in all the other Metazoa, Amphioxus and undoubtedly also the related genus Asymmetron [1]) stand isolated as remarkable in the whole animal kingdom.

It has been repeatedly attempted to declare the mouth of Amphioxus for a mesial organ by accepting that it has removed to the left side. Its occurrence in the larva on that side had then to be taken up as an abbreviation of development. This removal would then be analogous to the phenomenon observed in the eye of the Plenronectidae. The young larva of the flat-fishes has an eye on each side

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[1]) TATTERSALL (Notes on the Classification and geographical Distribution of the Cephalochorda. Proceedings and Transactions of the Liverpool Biological Society, Vol. 17, 1903) has shown that in the Homomeria (Acrania) we can distinguish only these two genera: Amphioxus (Branchiostoma) and Asymmetron.

and swims like all other fishes with its back up, the side-planes turned to right and left.

Later on however the animal swims with one side-plane turned up and the other down. The eye of the white under-surface then removes to the pigmented upper-surface, where the other eye is already situated.

An analogous explanation of the situation of the mouth in Amphioxus is impossible, because it becomes clear through the nerves and muscles of the displaced eye in the Pleuronectidae that this belongs to the under- and not to the upper-surface, on which it has come to lie.

The nerves and muscles on the inside of the mouth of Amphioxus, which all come from the left side, prove on the contrary, that it cannot be considered as a mesial organ, but in fact belongs to the left side.

While the mouth is formed on the left side in the young larva, a glandular metamorphosed gill-pouch, known as the club-shaped gland, arises opposite to it on the right side.

Its discoverer, HATSCHEK (1881), knew the external opening of this gland, but not yet the intestinal opening. Its presence was established by later investigators.

It was now clear that the mouth of the larva of Amphioxus could be considered as a metamorphosed gill-pouch, and as an antimere of the club-shaped gland.

The question however arises with which organ of the higher animals the left-sided mouth of the Amphioxus larva is homologous. Is it the homologue of the left half of the mouth of the Craniota, that would then have to be considered as a product of fusion of the mouth of Amphioxus with the club-shaped gland; or is the mouth of the Amphioxus larva the homologue of the first left gill slit of the Craniota, which is known in the Selachii as the left spiracle?

Various grounds led to the conclusion that the latter must be the case. To my mind this was proved when it was found that the body-cavity of the lower jaw, the mandibular cavity, does not in Amphioxus lie *behind* the larval mouth, as is the case in higher animals, but *in front* of it.

Amphioxus, indeed has no jaws, upper- as little as lower jaw, but still it has a mandibular cavity that indicates the position of the lower jaw. It is self-evident that an opening, arising behind the place of the lower jaw, cannot be considered a homologue of a part of the mouth of the Craniota.

Such a primitive organ as the mesial buccal opening of the Verte-brates must however originally have been present in Amphioxus. In my opinion the opening of HATSCHEK's groove, which is a product separated off from the fore-end of the intestine, must be considered as the primitive mouth of Amphioxus.

However this may be, the original mouth of Amphioxus must have been, just as in the higher animals, a symmetrical organ situated in the mesial plane, rostrally to the spiracle.

Why has the original mouth in Amphioxus been lost and been replaced by the left spiracle?

The manner in which the larvae that have just left the egg membranes move, can show us the way to come to an answer of this question. These larvae move forward spirally, by means of cilia, turning round the longitudinal axis from right to left. If we suppose that ancestors of Amphioxus possessed this form of motion permanently, then the left spiracle occurred in a more advantageous position to take in the sea-water necessary for nutrition and respiration, than did the mesially situated primitive buccal opening. This form of motion also makes the remarkable occurrence of the branchial apertures comprehensible. If we neglect the fore-most pair, which is metamorphosed to mouth and club-shaped gland, the gill clefts do not occur in successive pairs as in all the Craniota. On the contrary, the apertures on the right side are altogether wanting in the larva during the period of growth; they do not appear until during the metamorphosis. During the period of larval growth the clefts on the left side alone appear. They make their appearance successively to a total of 14 or 15, apparently however not on the left side but in the *topographical* mesial plane of the pharynx. Shortly after appearing each of these clefts is removed to the topo-graphical right side.

At first sight this phenomenon seems very extraordinary, but it becomes more comprehensible when we consider the location of the truncus arteriosus, which indicates in Amphioxus, as in the higher animals, the morphological mesial plane of the pharynx.

In the older larva of Amphioxus the truncus arteriosus does not run in the plane of symmetry under along the branchial intestine, but high dorsally along its right side.

The morphological right side has remained behind in development as a narrow dorsal strip in consequence of the excessive growth in breadth of the left side, which has hereby occupied the ventral territory of the right side.

Although the first 14 or 15 branchial apertures of the larva now

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lie on the *topographical* right side, they *morphologically* still belong to the left side. It is first in the following period, that of metamorphosis, that the right side of the pharynx also grows in breadth and gradually pushes the left side, with the gill-clefts back to the side where it belongs.

The right gill-clefts now arise for the first time, having earlier been hindered in their appearance by the crowding of the clefts of the left side.

With a screw-like motion turning from right to left such an occurrence of the gill-clefts is no longer odd. The secondary mouth of the larva takes up water that flows away through the gill-clefts by means of ciliary motion. The gill-clefts of the left side had now to remove [1]) to the topographical mesial line or better still to the topographical right side to prevent their taking in water.

In my paper of 1914 I mentioned already that the form of motion of the young larva can explain not only the origin of the mouth on the left side, but also the odd occurrence of the gill-slits. It was also mentioned that such a form of motion moreover makes it comprehensible that the organ of hearing (organ of equilibrium) could be lost, because the axis of a rotating object if the velocity be sufficient, is stable; while it cannot be expected in such a form of motion that the eye would be developed to a complicated organ, forming images.

At that time the criticism of ADAM SEDGWICK on my explanation of the asymmetric location of the mouth, in the third part of his text-book, published in 1909, was unknown to me. It is hidden in the chapter on the Echinodermata, in which the mouth originates symmetrically in the ventral median line, to remove later on to the left side.

Admitting that this case of secondary asymmetry differs from the phenomenon in Amphioxus, where the mouth is developed primarily asymmetrically SEDGWICK says that Amphioxus and the Echinodermata still have the left-sided location of the mouth in common. He continues (l.c. p. 162) "Here again we have a character which strikes us from its very rarity, for it is found in no other Coelomate nor so far as we know in any other member of the animal kingdom. It also strikes us by its strangeness and inexplicableness. In Amphioxus no serious attempt has been made to explain it".

My explanation was thus according to SEDGWICK *no serious attempt.*

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[1]) The removal of a mesially situated organ to the left side is not without analogy; it occurs e.g. in the heart and stomach of man. As the nerves of these organs arise from both halves of the body it is also clear, without knowing their development, that they must have been situated mesially.

He also gives his reasons: "for no one, so far as we know, has ever attempted to bring the extraordinary features in the development of the gill clefts, of the endostyle, of the head-cavities, the asymmetric position of the anus and olfactory pit, into relation with the asymmetry of the mouth. The thing cannot be done. There is no sort of connexion between these various asymmetries. They seem to occur without rhyme or reason".

Of all these arguments there is only one that seems to be consistent viz. that concerning the anus. We shall consider them consecutively.

An explanation for the removal of the gill-clefts to the right side has just been discussed. The thyroid gland, indicated by SEDGWICK by the antiquated name of endostyle, is a mesial organ in all the Chordata. In Amphioxus it must also originate in the morphologically ventral median line of the gut. We saw that this line has been shifted to the right side in the branchial region of the larva. In the larva with three open gill-clefts (LANKESTER and WILLEY, 1890, fig. 1) it runs over the topographically dorsal (but morphologically ventral) edge of the gill-clefts. If we continue it slightly rostrally it cuts the angle in which the two portions (the later right and left halves) of the thyroid gland meet. In the larva the thyroid gland thus lies topographically asymmetrically; morphologically however symmetrically.

The symmetry is in so far imperfect in that the lower portion (the later left half) is longer and reaches considerably further rostrally than the upper portion (the later right half). We shall make use of this difference later on in refuting another argument of SEDGWICK.

That the morphological median line of the gut was shifted to the right side also anteriorly to the gill-clefts viz. in the neighbourhood of the mouth can easily be explained by the considerable enlargement of the mouth, which takes place not only in the longitudinal, but also in the dorso-ventral direction.

In the latter direction its lower border all but reaches the topographically ventral median line, which it even passes during the metamorphosis, so that this typically left-sided organ is partly found, not *temporally* like the first gill-clefts, but *permanently* on the right side of the animal.

The thyroid gland cannot take its permanent place at the ventral border of the gut until during the metamorphosis, after the gigantic larval mouth has been reduced, temporarily even nearly to nil. Then the difference in length between its left and right halves has also disappeared.

SEDGWICK's third argument are the extraordinary phenomena in the development of the "head-cavities" i.e. of the portions of the coelom

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in the region of the head. The term "head-cavities" was introduced by BALFOUR, who discovered them in the development of the Selachii. In the branchial region of Amphioxus the coelom is divided by the gill-clefts into as many "head-cavities" as there are clefts, and the asymmetry of these cavities necessarily coincides with that of the gill-clefts. Here there is no new oddness to be explained.

But SEDGWICK (textbook part II, 1905, p. 34) wrongly understands under "head-cavities" only the foremost entoderm sacs of HATSCHEK, which are placed before the mouth, as it seems, as each others' antimeres. Soon however they take up a mesial position, whereby the right sac, a true head-cavity, is shifted before the left. In its further development the left sac has not a single character from which it could be deduced that it should be considered as a section of the coelom. Since 1893 — the last time more in extenso in 1914 (l.c. p. 63) — I have defended the opinion that the two sacs are only *apparent* antimeres, that they originally must have lain not opposite to, but before each other, and that the apparent antimeric occurrence must be the result of the asymmetry of the larva. In this opinion I however remained alone. The later investigators attached so much importance to the first appearance — certainly an argument of great weight — that they did not consider the important differences which soon arise. Undoubtedly the symmetrical situation of the foremost myotome (which must be considered as the second of the row; the first is included in the right entoderm sac) played a role in this. Yet in the rest — with exception of the third of the row — each myotome of the left side reaches, since its first appearance, half the length of a myotome more rostrally than its antimere of the opposite side.

As this wry symmetry is found only in the region behind the mouth, in front of it however not, it was apparently taken for granted that the true gut in the snout would indeed be properly symmetrical. This is however not the case.

When the first gill sacs of the right side make their appearance during the period of metamorphosis, the foremost of these does not lie opposite its antimere, but opposite the second gill cleft of the left side (cf. my paper 1914, fig. 3, 4, 5). In the fore-end of the branchial region the left side of the gut has been displaced rostrally over the whole length of a branchial metamere. [1])

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[1]) In the adult animal, (and also in the more caudally situated clefts of the larva) this removal is not so large. The foremost half of a left cleft then, as is known, does not lie the whole, but half the length of a cleft rostrally to its antimere of the right side.

This removal also reaches to the part of the gut situated before the buccal aperture, as is evident from the above-mentioned (p. 1017) difference in length of the two portions of the thyroid gland, whose lower (later left) portion reaches much further forward than its upper (later right) portion (cf. my paper 1914, fig. 1, 2, 3 out of the metamorphosis and LANKESTER and WILLEY 1890, fig. 1 of a young larva with 3 open gill clefts).

As the entodermsacs of HATSCHEK now arise opposite each other just in front of the region of the thyroid gland the conclusion is obvious that their antimery is only apparent, even if we pay attention to their first appearance only, without considering their subsequent fate: The left sac is removed forwards and ought morphologically to lie behind the right sac, as is indeed the case later on.

The last arguments of SEDGWICK are the asymmetrical situation of the anus and the olfactory pit.

The removal of the olfactory pit, which develops out of the mesially situated neuroporus, to the left side is easily explained by the spiral motion with rotation of the axis from right to left: The olfactory pit had to catch up water and therefore to remove to the left side.

The asymmetrical situation of the anus could however not be explained so easily. Not only does it lie on the left side in the adult animal, but according to HATSCHEK (1881) it is already situated on that side in the young larva with one gill cleft.

In the same way as the gill clefts serve for letting out the water taken up by the mouth of the animal, the anus serves for letting out the undigested food. The respiratory water as well as the faeces are propelled not so much by muscular contractions as indeed principally if not exclusively by ciliary motion, thus by weak forces.

To the same extent as it was profitable for the gill clefts to remove to the right side one would also expect this in the anus. It would have to be considered as a postulate of the theory that the anus either originated in the mesial plane, to remove later on, not to the left, but to the right side, or that it developed directly on the right side.

In the hope of being able to discover something in young larvae that would throw some light on the question, I found beyond expectation, that the anus in larvae with one gill cleft is situated not on the left but on the right side of the body.

This was clear beyond the slightest doubt in series of cross sections. In preparations in toto it was however impossible, even with the strongest dry lenses, to determine in such a young larva on

which side of the body the extremely fine anal aperture was situated, because it could only be observed in profile, thus by focussing the microsope alternatively.

After however using strong oil-immersion systems (e.g. Zeiss obj. $^1/_{12}$ oc. 4) the situation of the anus on the right side of the body could clearly be seen also in these preparations.

When the anus has just made its appearance the tail-fin does not yet reach rostrally to it, but this is soon the case, even when there is only yet one gill cleft present. The anal aperture then lies on the right side of the tail-fin. Here it is also found in larvae with 2, 3, 4, 5 or 6 gill clefts.

Now however the remarkable phenomenon presents itself that it removes to the left side. In larvae with 7 gill clefts a lacuna arises in the tail-fin at the level of the anus, so that the tail-fin is inter-rupted at this place. The anus now enters this lacuna and thereby assumes a mesial position in relation to the body. This position is however of short duration. With the presence of 9 gill clefts the anus has already passed over to the left side, where it is further permanently found. The lacuna in the tail-fin vanishes and leaves no traces of its former existence.

I cannot give a reason for this removal. It must stand in con-nection to the manner of life, of which we know little or nothing. This does not however affect the principal question, the original situation on the right side, as it was postulated by the theory.

If the theory is not accepted then there is here especially occasion for speaking of a development "without rhyme or reason".

In the theory there is in any case a "reason" for the initial situation of the anus even if it cannot "rhyme" its permanent position with this fact.

The question whether a pancreatic gland occurs in Amphioxus does not stand in relation to the asymmetry discussed above.

This gland is known in all the Craniota, from the Cyclostomata to man, but it is the common opinion that it is not present in Amphioxus.

It arises in the Craniota as one or more bulbs protruded out of the gut epithelium in the immediate neighbourhood of the aperture of the ductus choledochus, which as a rule later on also forms an opening of the pancreas.

In the Lampreys, which in connection with Amphioxus must be considered in the first instance, the gland is not very voluminous. This must partly be ascribed to the fact that their pancreas, like

the liver, officiates as an organ with internal secretion. The excretory ducts of these glands, as well as the gall-bladder, have disappeared after the metamorphosis, but in the Ammocoetes, the larva of the Lampreys, they are present.

The pancreatic gland of Ammocoetes lies hidden in the wall of the gut on the left side of the excretory duct of the liver.

At a quite analogous place I found the gland in Amphioxus from the first appearance of the liver in the period of the metamorphosis until the adult form. With good nuclear staining it can be seen, in preparations *in toto* of the newly metamorphosed larva, as a triangular stain on the left side of the wall of the gut immediately behind the place where the blind sac of the liver emerges. The rounded top of the triangle points forwards, the base is a transverse line, crossing the longitudinal axis of the animal at right angles. With a strong magnification it can be seen, more clearly still in cross section, that we have to do with a slight emergence of the wall of the gut.

In the sections we see that the gland possesses a strong ciliary epithelium, but it has moreover cells without ciliae which may be considered as the true glandular cells. In the adult animal the gland is stretched more longitudinally, and consequently the emergence of the gut wall is a longitudinal fold; its fore-end has been taken up in the hind-end of the blind liver sac. We find an analogous phenomenon in some fishes, where the pancreas is partly enveloped by the liver.

The reason why the numerous investigators of the anatomy of Amphioxus could not find a pancreas is easily given. The mid-gut epithelium presents in cross section so many folds [1]) that it cannot be expected that one could distinguish these from the pancreatic fold unless one's attention has been drawn to this in young animals.

In the ontogenesis of the Craniota the liver (as an emergence of the gut) is first recognisable; somewhat later also the pancreatic gland. In Amphioxus this is just reversed. While the liver first makes its appearance as an emergence of the gut in the period of metamorphosis, the pancreatic gland can be followed back to the stage with two open gill clefts (in larvae with only one gill cleft it could not be seen). It is originally not limited to the left side, as is later the case, but envelops the gut like a ring. The ring is recognisable in that its nuclei are smaller and placed closer together

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[1]) These folds are also found in the oesophagus, (whose hind-end corresponds morphologically to the stomach of the higher animals', and in the foremost portion of the end-gut. They serve for enlarging the resorbant surface. In young animals they are not present.

than is the case before or behind the gland. The ring however is not regular, but its left side is developed more strongly than the right. Soon however it disappears on the right side and through this the gland becomes asymmetrical.

As this asymmetry is also found in higher forms e.g. Ammocoetes, it must be independent of the above discussed asymmetry of the branchial gut.

Finally I should like to point out that another gut-ring the ilio-colon ring, in the larva with one gill cleft is of importance for the morphology of the alimentary canal in the Vertebrates. In Amphioxus this ring indicates the boundary between mid- and end-gut.

Physiologists have already long known that the nervus vagus in the higher animals and man helps to supply not only the fore- or "head"-gut, but also the whole mid-gut or "small intestine". Anatomists as a rule ascribed to the n. vagus the region of the fore-gut only, because the foremost of the two strands which form the continuation of the vagus plexus around the oesophagus, ends on the foremost wall of the stomach, while the hindmost strand is connected with the plexus solaris of the sympathetic nerve.

On account of this connection it was impossible to follow with certainty the ramifications of the vagus further distally than the stomach. Our countryman DONKER [1]) has however lately succeeded in doing this in apes. He could establish the fact that the ramification of the vagus reaches to the end of the mid-gut and that it does not extend to the "large intestine" (end-gut in a broad sense). In the section of his text-book which appeared this year MERKEL also lets the ramification of the vagus in man reach to the end of the mid-gut.

It is not surprising that the vagus, the tenth cranial nerve, supplies the fore-gut as it is a well known fact that the fore-gut is originally limited to the head region. The question now arises whether the mid-gut was perhaps originally situated in the head region also. To a certain extent the development of Amphioxus can give us an answer to this.

The ilio-colon ring, which forms the boundary between mid-and end-gut lies more rostrally the younger the larva is. The larva of LANKESTER and WILLEY with 14 gill clefts already has 61 myotomes, just as many as the adult animal. The ilio-colon ring lies under the 34th, 35th and 36th myotomes. In their larva with 3 gill clefts and only 36 myotomes the ring lies under the 15th and 16th myotomes.

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[1]) P. DONKER, Ueber die Beteiligung des N. vagus an der Innervation des Darmes. Anat. Anzeiger, Bd. 51, No. 8, 1918.

In the Selachii and, indeed, generally in the Craniota the first 9 myotomes belong to the head. It would now be interesting to know under which myotome the ilio-colon ring of Amphioxus is situated at its first appearance. This appearance takes place in the stage with only one gill cleft and an open anus.

Although in the course of time I have made hundreds of preparations of this stage, stained and imbedded in all sorts of ways, I have not been able to count the number of myotomes. Their boundaries, which are clearly discernible in earlier and later stages, were not visible in this stage, not even in series of sections [1]).

It is possible that these boundaries are to be seen in living larvae. In any case HATSCHEK (1881, fig. 64) indicates in a sketch of such a larva that there are 20 myotomes present; the ilio-colon ring has however escaped his notice. If now the place of this ring, which is very clear in my preparations, is compared with the sketch of HATSCHEK, one comes to the conclusion that it must be situated approximately under the 9th myotome, thus at the end of the head region.

In other words: Not only the fore-gut (prosenteron) but also the mid-gut (mesenteron) originally lies in the head region, and if this is also the case in the Craniota, as may be expected, then it is no wonder that also the mid-gut is supplied by a cranial nerve, the n. vagus. The conception "head-gut" ought then not, as is at present the case, to be synonymous to fore-gut, but must include the mid-gut also.

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[1]) One could speak here of a cryptometameric stage, a characteristic — amongst others — that these larvae have in common with the Appendicularia and the larvae of the Ascidians, in which the metamery is at present still denied by various investigators.

Anatomy. — *"Is the post-embryonic growth of the nervous system due only to an increase in size or also to an increase in number of the neurones?"* (Second part). By Erik Agduhr. (Communicated by Prof. J. Boeke).

Mitoses.

In connection with these matters I have found specially interesting phenomena in the thoracic region of a puppy seventeen days old. The spinal ganglia were fixed according to Flemming's method, cut up in paraffin sections from $3\,\mu$ to $5\,\mu$ thick and stained with the iron alum hematoxilin of Heidenhain. In these continuous series of sections I found a large number of mitoses — an approximate calculation showed that in a single one of these ganglia there were over two hundred mitoses. Figures 5, 6, 7, and 8 show how these mitoses appear in the preparation. One would be inclined at first sight to refer these mitoses, especially the ones reproduced in figures 5 and 6, to the large ganglion cells — the light field round the chromatin showing, of course, a rather diffuse transition to the rest of the protoplasm. Owing to the continuous series I was able, however, to follow the cells from one section to the other, and then I found that the real nuclei of these ganglion cells were not found in a stage of division, and that these mitoses must belong either to other small cells situated between the ganglion cell and its capsule or probably to cells that form the capsule itself. In fig. 7, on the other hand, merely from the sharp outline which the light field makes against the surrounding protoplasm it is clear that there can be scarcely any question of the existence of a mitosis in the ganglion cell — this was also confirmed by the investigation of the same ganglion cell in the preceding and following sections. In fig. 8 we have again an example of a cell which is going to divide mitotically, and which is situated outside the capsules of the surrounding ganglion cells. With regard to size it resembles most closely the cells in mitotical division in figures 6, 7, and 8, but on closer examination, for instance, if they are traced from section to section, one finds that it is surrounded by capsule cells. We thus seem to be quite justified in describing

this figure as a spinal ganglion cell at such an early stage of development that it had not lost its power of increasing in number through mitotical division. I found another mitosis of this kind in the series just mentioned. Among the other group of mitoses, namely those in cells that are situated inside or in the capsule of an older ganglion cell, my preparation shows at least a few forms in which one can clearly follow the capsule peripherally of the cell that is engaged in mitotic division and where the latter must therefore be situated beneath the capsule. There are thus good reasons to support the assumption that, even among this group of mitoses, some are to be referred to very young undifferentiated cells, which on good grounds — for instance on account of their position — can be assumed to develop into nerve cells. By far the larger number of mitoses are, however, undoubtedly to be referred to ordinary capsular cells. But is the difference between the capsular cells and the nerve-cells really so great? Are not the former perhaps to be regarded as matrix cells for the latter? I must leave these problems to a subsequent and more detailed account of this question and confine myself to saying that there are points in the preparation that support such an assumption [1]). These facts are all the more worthy of attention because, among the investigators who formerly looked for mitoses in spinal ganglia, FLEMMING [2]), DAAL and LENHOSSEK have been unable to show any in young animals. MÜLLER [3]), on the other hand, found them in new-born animals, but in no later age. The very large number of mitoses in the spinal ganglia shown in the present and other investigations of young animals clearly support the considerable post-embryonic increase in the number of capsular cells in this region, an increase that could scarcely be explained if the ganglia did not increase in number too. In my opinion the exceedingly great number of mitoses that are found in the spinal nerve-cells, according to what has been shown above, cannot possibly be explained by an increase in size merely of those spinal nerve-cells which were already present at birth. This is the less probable because the spinal ganglion-cells must decrease in number with the years, if new ones do not grow out and replace all those that degenerate and die away during post-embryonic life. And this degeneration of the nerve-cells is admitted and shown by all the chief investigators of this problem.

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[1]) See addendum!

[2]) FLEMMING, DAAL and LENHOSSEK. Quoted from MÜLLER E.

[3]) MÜLLER ERIK, Untersuchungen über den Bau der Spinalganglien. Nord. med. Ark. Stockholm. Bd. 23. 1891.

That such degeneration is rather common is also proved by the fact that no slight number of cells in a spinal ganglion of even a young animal show signs of degeneration. The new growth in this region has thus the task not only of replacing the ganglion-cells that have been destroyed by degeneration, but also of increasing their number. A fairly considerable increase of this kind takes places, as is shown above, during the animal's period of growth. To judge from my preparations, nature seems in this generation to make use of both mitotic and amitotic division. In no case have I been able to refer the cells that show the latter type of division to such small forms as those in which mitoses occur; the former cells seem to belong to remaining ganglion cells that are somewhat older and sometimes, at least, with a certain degree of development, for I have been unable to find fully developed processes among them.

Amitoses.

Besides the figures of mitoses one also sees in the preparations in question figures of cells which produce a strong impression of being engaged in direct division. As shown below one sees cells that seem to be in different stages of this division. The cells of this type, however, always belong to the young ones, to those cells (in the silver-impregnated preparations) that have taken a very slight amount of silver or even none at all during the impregnation.

The different stages of a direct division which are found in my preparations appear as follows: One sees cells, in which the nucleolus is being divided or has just divided (fig. 1a and fig. 2b) and where the two nucleoli are still in each other's immediate neighbourhood. The two nucleoli then move away from each other and the nucleus begins to show signs of incision in the middle (see fig. 3b and fig 2b). After this there follows a complete division of the nucleus, which is also frequently accompanied by a division of the protoplasmic body, fig. 3a and fig. 2a. Fig. 3a must be interpreted as a young apolar ganglion cell in which, after the nucleus had first divided into two, the protoplasmic body began to divide in the middle, after which the two nuclei again began a new division. The preparations in which these observations were made were particularly well fixed and impregnated, so that it is fairly certain that there was no possibility of artificial products. Another thing that further supports the idea of natural formations is the fact that these figures above-mentioned do not occur in such very great numbers. It is true that there are many nuclei of ganglion cells (among the smaller ones) which have two

or more nucleoli, but there are fewer that show signs of division.

I shall discuss at greater length below some of the literature concerning direct post-embryonic division of nerve-cells. I will only mention here that RODHE[1]) describes four different types of amitotic division of the ganglion cells in full-grown evertebrates. PALADINO states that direct division is a very common way for young ganglion-cells in the higher vertebrates to increase.

In fig. 4*a* I reproduce a group of nerve-cells from a silver-impregnated spinal ganglion in a sixty days old puppy. In it the cells are packed close together into a formation shaped like a string of beads, lying within the same capsule. Between the cells at a few places one can also clearly see bridges of protoplasm, which connect cells that are close to each other. The series of sections of the spinal ganglia from this animal show numerous examples of similar groups (MÜLLER E.) of cells situated within the same capsule. I have obtained the impression, however, that they do not occur in equally great numbers in all the spinal ganglia of the same individual; similar groups of cells have been observed in puppies of six and seventeen days — but they were not so numerous as in the sixty days old animal [2]). In the 3,5 years old dog, among five spinal ganglia that were investigated, I did not come across more than a few of these groups of cells and in the five years old dog among a still greater amount of material, I did not succeed in finding such a group in more than a single place. It is thus an obvious assumption to regard these groups of cells as formations belonging to the post-embryonic growth of the spinal ganglia — forms produced by the spinal ganglion cells during the post-embryonic increase in their number.

In spite of the considerable number of works that have been published on spinal ganglia in the course of years, the information about these groups of cells to be found in this literature is exceedingly small. Before 1880, however, they had been observed by a number of investigators and were described most thoroughly by P. MAYER[3]). After that the subject seems to have been almost forgotten, until in 1889 and 1891 MÜLLER ERIK[4]) gave more thorough and valuable descriptions of similar groups of spinal ganglion cells within the same capsule. Since MÜLLER's description of these groups of nerve-cells they seem to have been neglected again in recent

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[1]) RODHE, Ganglienzellkern and Neuroglia. Ein Kapital über Vermehrung and Wachsthum der Ganglienzelle. Arch. f. mikr. Anat. Bd. 47.

[2]) The sixty days old dog was rachitic.

[3]) MAYER, S., Arch. f. Psychiatrie, Bd. 6, 1876.

[4]) MÜLLER, E., L c.

literature — I have not found a single mention of them in a whole series of recent publications on this subject that I have looked through. Müller gives the name of *"Cellkolonien"* to these groups of nerve-cells and distinguishes between regular and irregular colonies. "Die ersteren" — the regular ones — "sind nach aussen durch eine cirkelrunde Kapsel vom selbigen Aussehen wie diejenige, welche die grossen Zellen umgiebt, begrenzt; innerhalb dieser Kapsel finden zich zwei, drei oder vier Zellen sehr regelmässig wie Sectoren um einen Mittelpunkt geordnet". Müller also found bridges of protoplasm connecting the different cells of the colony with each other. I have not found in my preparations any colonies of cells which showed this regular arrangement of their cells, resembling a sector of a circle, although there are several figures of colonies in which the cells are very nearly equal in size; but in these cases they are situated side by side, although they do not always form such long rows as the one shown in fig. 4. Most of the colonies observed by me are quite clearly built up of cells that are different in size, and it seems as if one might place them all in the group that Müller describes as *irregular*. With regard to the significance of these colonies Müller writes: "Vielleicht steht das Vorkommen dieser Bildungen mit Regenerations-phänomenen in den Spinalganglien in Verbindung", but he points out that, as he had no opportunity of studying the processes of these cells, his statement on this point can only be a supposition. He continues: "So viel geht jedoch aus dem unbedeutenden Vorkommniss bei älteren Thieren von diesen Bildungen — Kolonien und Halbmonden — welche bei jungen Thieren zahlreich auftreten, hervor, dass sie Entwicklungsstadien von Ganglienzellen repräsentieren und ferner, dass die Entwickelung der Spinalganglien eine langsame ist, welche erst in späteren Zeiträumen von dem Leben des Thieres abgeschlossen wird."

In tearing preparations of older animals the same investigator found that the crescent-shaped cells that are situated within the same capsule as other ganglion cells, have no processes. These observations of mine, however, are not made from tearing preparations, in which one has of course always to reckon with the possibility of the removal of processes that have really been present, but are made from continuous series of intensely impregnated Bielschowsky-preparations, in which one can very easily look for these colonies section by section. In the series of sections from which fig. 4 is taken there is no trace of any processes. The spinal ganglion in question is intensely impregnated according to the method mentioned above. The impregnation is very successful; not only the axons,

but the neuro-fibrils appear exceedingly distinctly. One may thus postulate that if processes of the cells in this colony had really existed, they would also have clearly appeared in the sections. That these cells are likewise at an early stage in their development is indicated, in addition, by the fact that there are evident bridges of protoplasm between some of them. In this series of sections there are, however, colonies of cells which, as far as one can judge, are at later stages in their development — in these the different cells have processes, there are no bridges of protoplasm between them, and the future capsules of the separate cells exhibit the first traces of their development. In the cells of some of the colonies found in the 3,5 year old dog I have been able to show processes — there were also signs showing that these colonies were at a later stage of development than the one shown in fig. 4. In the five year old dog, as has been mentioned above, I found only a single colony of cells and no apolar cells. The results of counting the ganglion cells and their axons indicate, however, that there really are apolar cells here as well[1]). The purely morphological observations in the 3.5 and 5 year old dogs do not, of course, quite exclude the possibility of there being colonies of cells here as well at a very early stage of development, but with regard to this they indicate that in older animals these formations are relatively very rare. It is to be noted that such eminent investigators as KEY and RETZIUS[2]), SCHWALBE[3]) and of recent years RANSON[4]), are decidedly against the opinion that apolar cells are to be found in the spinal ganglia on the other hand. KÖLLIKER[5]), MÜLLER[6]) and others hold the opinion that such cells really exist. It would lead me too far from my real subject were I to discuss in detail the literature concerning apolar cells in the spinal ganglia. I must content myself with the references already given, and in connection with this point I wish to state that there are also investigators who have observed processes from cells in colonies similar to those described above; such are ARNDT[7]) and STIENON[8]) etc.

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[1]) These and other explanatory details will be given more fully in a forthcoming and more complete work.

[2]) KEY and RETZIUS. Studien in d. Anat. d. Nervensyst. u. Bindegewebe, Bd. 2, 1876.

[3]) SCHWALBE, Arch. f Mikr. Anat. Bd. 4; 1868.

[4]) RANSON, L. c.

[5]) KÖLLIKER, Handbuch der Gewebelehre, 5 Aufl., 1867, quoted from MÜLLER E.

[6]) MÜLLER, E., l. c.

[7]) ARNDT, Archiv f. Mikr. Anat., Bd. 10, 1873.

[8]) STIENON, Annales de l'université libre de Bruxelles, 1880, quoted from MÜLLER E.

If now we summarize the observations that have been made and given above on these colonies of cells and the processes of the cells that belong to them, it seems to be clearly shown *that some at least of the apolar cells in these colonies grow out to new neurones during the postembryonic growth of the animal.* On the other hand it does not seem to me so easy to decide how these colonies of cells arise. The way is perhaps that small cells from the capsule cells which have been developed mitotically, or are at least situated within the capsule, grow out into new ganglion cells, which are added to other ganglion cells already existing within the same capsule. Might not a relatively large ganglion cell, which in some respects is at an earlier stage of development — for instance, apolar — increase in number and become one of these colonies of cells by means of amitotic divisions. I have not been able to decide with certainty whether one or the other or both of these methods of formations occur, though, as a matter of fact, there are signs in my preparations to support the idea that both these methods of formation may occur.

If, as seems to be shown above, a new formation of neurones in the spinal ganglion really occurs post-embryonally, one would and might, of course, also expect to find, during post-embryonic life, figures of growing axons in the peripheral nerves. I have examples of such claviform figures, which are quite evident in silver-impregnated preparations of, for instance, the dorsal and ventral roots of young dogs. More details of this will, however, be given below.

I consider that I have now shown that the cells in the spinal ganglia sufficiently explain the origin of the actually existing and fairly considerable post-embryonic numeric growth of axons in the dorsal roots of the spinal nerves. I shall now pass on to examine to some extent in connection with those matters the

Medulla spinalis.

There is but exceedingly scanty information about post-embryonic divisions of the ganglion cells of the central nervous system to be found in literature, and the existing accounts are not generally admitted to be correct. These accounts, however, take two directions. Some investigators maintain that the cells in this region divide by means of mitoses, others say that the usual method of increase in this case is that of amitotic cell division.

Mitoses.

ALLEN[1]) states that in the spinal cord of an "albino rat" twelve

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[1]) ALLEN, EZRA. The cessation of mitosis in the central nervous system of the *Albino rat;* J. Comp. Neurol. Vol. 22, pp. 547—568, 1912.

days old he found (counting in mm³) 46 mitoses in the cervical, 75 in the thoracic and 14 in the lumbar region, but that in an animal twenty days old he could not show a single one.

HAMILTON[1]) found in thirteen succeeding sections, 6,75 μ thick, from the medulla spinalis of a four days old rat mitoses in the ependyma and 64 situated extraventricularly.

ADDISON W. H. F.[2]) found in an "albino rat" nearly 22 days old mitoses "in the other granule layer" of the cerebellum.

SCLAVUNOS G.[3]) has observed mitoses in the central nerve system of new-born dogs.

SUGITA NAOKI[4]), who has studied the post-embryonic growth of the cortex of the brain in the "albino rat", found that the value for the number of cells in this region in the ten days old animal was $1,9 \times$ the value at birth, and that the number of cells increases further during the next ten days and is complete at twenty days. After this time the number of cells is practically constant and the number of cells in the fully-grown state is approximately twice as great as at birth. These calculations are based on the determination of the number of cells in only two layers at only one place and therefore their general value may be questioned. S. has, however, previously shown by measurements made at different places on the cortex of the brain that it undergoes the same relative increase in thickness between birth and maturity. S. considers that the values obtained may therefore with great probability be generalized for the whole cortex. With regard to the way in which such a post-embryonic increase in the number of cells in the cortex takes place one can, of course, herein supported by ALLEN, who in 25 days old specimens of the "Albino rat" found as many as 27 mitoses per mm³ of tissue in the cerebrum, consider that it is due to mitotic division.

The values given for the number of mitoses and for the increase in number of the cells in the central nervous system do not refer to any definite number of cells, but apply to all the cells taken together, and thus do not exclude an increase in the number of

[1]) HAMILTON, ALICE, The division of differential cells in the central nervous system of the white rat. J. Comp. Neur., Vol. II, pp. 297—320, 1901.

[2]) ADDISON, W. H. F., The development of the *Purkinje* cells and of the cortical layers in the cerebellum of the *Albino rat*. J. Comp. Neurol. Vol. 21, pp. 459—487.

[3]) SCLAVUNOS, G., Ueber Keimzellen in der weissen Substanz des Rückenmarks von älteren Embryonen und Neugeborenen Anat. Anz., Bd. 16, 1899.

[4]) SUGITA NAOKI, Comparative Studies on the growth of the Cerebral cortex III, IV and VI, Journ. Comp. Neur. Vol. 29, 1918.

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both glia and ganglion cells. The mitoses found in the central
nervous system of young animals do not seem to refer to so-called
neuroblasts (HIS) [1]), but the preparation indicates that KOELLIKER [2])
is right when, partly by reasoning and partly by direct observations,
he comes to the conclusion that those "Keimcellen" that are in
mitosis are undifferentiated epithelium-cells, which give rise to both
glia and ganglion cells. SCHAPER [3]) arrives at the same result by his
investigations of the course of differentiation in the central nervous
system of the trout. We thus seem to be justified in postulating as
a fact that as long as mitoses can be shown in the central
nervous system a new formation of ganglion cells is also taking place.

In PRENANT [4]) we read as follows: *a*. "Les cellules nerveuses, en
se différenciant, ont perdu le pouvoir de se reproduire, *b*. Les rares
multiplications qu'il a été possible d'observer dans les cas de cicatri-
sation de portions du névraxe, appartiennent à la neuroglie (VALENZA,
MARINESCO, MONTI); *c*. Enfin il n'est pas exclus que les quelques mitoses
observées doivent également être assignées à la neuroglie". Among
the investigators who do not seem to be able to admit the possi-
bility of an increase of the neurones during post-embryonic life I
want to mention also BIZZOZERO [5]) and MARINESCO [6]). In deciding such
matter these authors seem more or less to have proceeded from the
idée préconçu that the neurons have a very long life and
are nearly perpetual. They consider that this is an absolutely neces-
sary qualification if the individual is to perserve its psychical
inheritance, to form associations of ideas, and for memory in general.
A close study of suitable preparations of, for instance, the spinal
cord from animals of different ages will soon convince us that
this does not quite agree with the real facts. For in these
preparations one finds not infrequently figures of ganglion cells
which are degenerating as well as those which indicate generation.
Nor is the literature on the subject without scattered statements
about observations of such degeneration in the central nervous

[1]) HIS, Die Neuroblasten und deren Entstehung im embryonalen Mark. Arch f.
Anal. u. Entwickelungsgesch. 1889.

[2]) v. KOELLIKER, Gewebelehre, Bd. 2, 1893.

[3]) SCHAPER, Archiv. für Entw. mech. der Organ. Bd. 5.

[4]) PRENANT, Histologie et Anatomie microscopique, t. II, p. 353, 1911.

[5]) BIZZOZERO, G , Accrescimento e rigenerazione nell'organismo (Conferénce du
Prof. G. BIZZOZERO au Congrés international tenu à Rome en 1894). Voir, en
outre, dans le 2e volume des oeuvres scientifiques du même auteur publié a Milano
en 1905, et dans les Arch. ital. de Biol. t. XXI, p. 93, quoted from PALADINO.

[6]) MARINESCO, G., La cellule nerveuse, Vol. 1, p 400, Paris 1909.

system. Among the investigators who have made such observations we mention RETZIUS, v. GEHUCHTEN, RAMON Y CAJAL, DEJERINE.

The presence of degenerating nerve elements in individuals that are growing also renders the possibility of a regeneration of such very probable. If there is no regeneration, the nerve elements would, of course, decrease during growth—a phenomenon that is not indicated by any recorded observations. The probability of generation becomes certainty, however, when one investigates suitable preparations from the central nervous system, for instance from the spinal cord of animals at various post-embryonic ages. Such preparations show numerous figures of new growth, which seem to me sufficient to explain not only how degenerated ganglion cells are replaced, but also how the increase in nerve fibres in the central roots arises, which I proved above to exist during the period of growth.

I have made suitable preparations for these investigations from the spinal cord of toads, mice, rats and dogs of different post-embryonic ages. The material was fixed either in FLEMMING's or ZENKER's fixing liquids and the paraffin sections cut from it were impregnated either with HEIDENHAIN's iron-alum hœmatoxylin or with ERLICH's acid hœmatoxylin. I have in addition, quite excellent BIELSCHOWSKY-preparations from this material.

In the hœmatoxylin-impregnated preparations from toads 2 cm. long (from neck to sacrum) and ten days old mice I found some — but very few — mitoses. On the other hand I have not found any certain examples of such mitoses in the older individuals of this species nor in six and seventeen days old dogs or in full-grown ones. In a young mouse 23 days old (*Mus musc. var. albus*) I found three appearances, which are reproduced in figs. 9 and 11. The figures are carefully drawn from preparations — which are from the material that was fixed by FLEMMING's method — and, at the first glance, certainly produce the impression of being mitoses, and it is possible, of course, that this is the case. A number of facts seem to me, however, to render this doubtful; these are first, that I have not found any more mitoses in this animal and, secondly, that in other mice of equal age, in which the material was fixed according to ZENKER's method — this method gave better and finer results — and impregnated in the same way, I have not found any trace of mitoses. In any case I have not found any appearance of a mitosis in preparations of the spinal cord of white mice more than 24 days old. My observations of mitoses in the spinal cord of growing individuals thus agree on the whole with those previously made by other in-

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vestigators. As far as the animals investigated by me are concerned, an increase in the number of neurones by means of mitotic division of nerve cells seems thus to be concluded during the first month of post-embryonic life. DONALDSON's [1]) statement: "Moreover, in the case of the albino subjected to modifying conditions after 30 days of age, *the number of neurones is already complete at this age, so that the changes induced are again merely of size* [2]), unless some neurones should have been destroyed," is an assertion that I cannot agree with, as far as my material is concerned, and I am inclined to think that it does not describe the conditions in any animal. If one gives a strict definition of a neurone as being a nerve-cell with its processes, one of which is an axon and the others dendrites, and one adds to this the generally accepted condition, which by means of the evidence put forward about it, has almost become a certainty, namely that one cell in the ventral horn does not send more than one axon out into the ventral root and that the axons do not show any T-division on their way through this root, the considerable post-embryonic increase in the number of axons in this region, which has been shown above to be an actual fact, is a proof of the real existence of an increase in the number of neurones during a considerably longer period of development than the one given by DONALDSON.

The Wistar school (DONALDSON and others) have, as has been stated above, with their splendid statistical and experimental investigations found, by means of the methods they have used (staining of medullary sheaths), that post-embryonic growth in the nerve roots is principally merely an advancing myelinisation. The most important of all the changes that take place during this process, namely the post-embryonic growth in the number of axons, has quite escaped their notice. There was therefore no need to look for an increase in the number of neurones going on for a longer time postembryonally than the time during which the mitosis in the central nervous system showed clearly that an increase of this kind really existed. But is mitosis the only way in which an increase or a new formation of the cells in the central nervous system can take place?

Scattered statements in the literature exist to the effect that a new formation of nerve-cells may also take place by means of

[1]) DONALDSON, H. H., HATAI, S. and KING, H. D. Post-natal growth of the Brain under several experimental conditions. Studies on the albino rat. Journ. Nerv. and Mental Disease. Vol. 42, 1915.

[2]) The italics are mine.

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ERIK AGDUHR: "Is the post-embryonic growth of the nervous system due only to an increase in size or also to an increase in the number of neurones?"
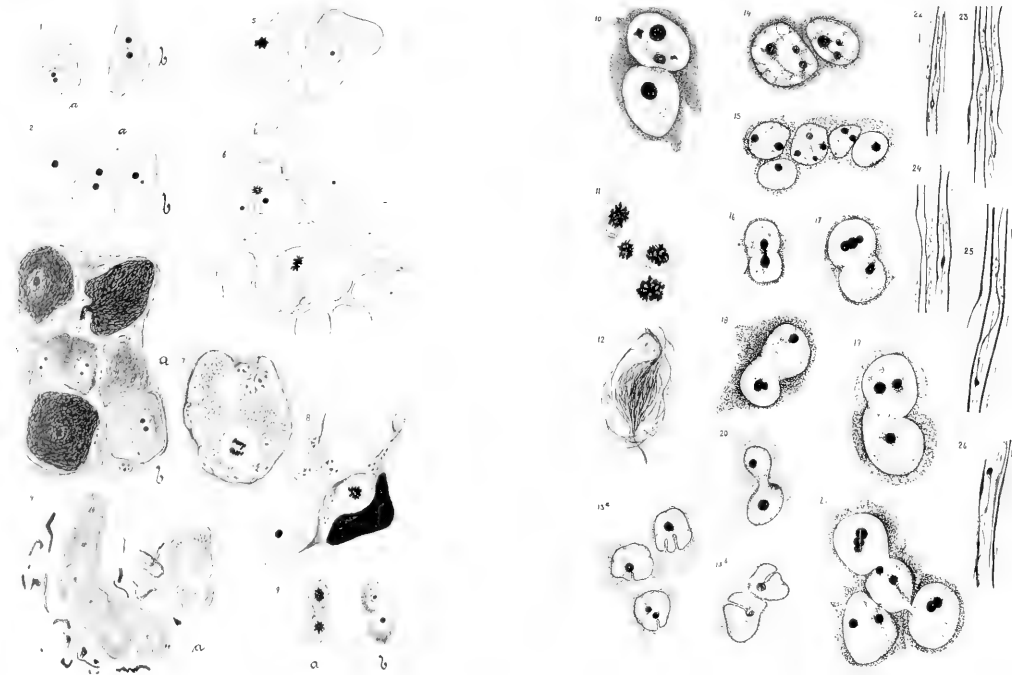
EXPLANATION OF FIGURES

Figures 1, 2, 4, 5, 6, 9, 10, 11, 22, 23, 24 and 25 are drawn after magnifying with LEITZ immers. ⅟₁₂ and ocul. 4 and using REICHERT's drawing apparatus

Figures 3, 7, 8, 12 and 26 are drawn after magnifying with ZEISS apochr. immers.; 2 mm. Apart. 1.3 and Comp. ocul. N°. 6, with the help of Abbe's drawing apparatus

Figures 13, 14, 15, 16, 17, 18, 19, 20 and 21 are drawn after magnifying with ZEISS Apochr. imm., 2 mm. Apart. 1.3 and Comp. ocul. N°. 12, with the help of LEITZ's drawing apparatus

Fig. 1. Repr. ⁷⁄₁. Gangl. spin. (Fix. FLEMMING staining Jhtx and Eos) of a 17 days' old dog. a Ganglion cell with division of the nucleolus just started b Nucleus dividing amitotically. This small distinct collum-formation between the nuclei is very rare.

Fig. 2. Repr. ⁷⁄₁. Gangl. spin. (Fix. and staining the same as the preceding) from the same section series as in fig. 1. a. Ganglion cell dividing amitotically. b. Ganglion cell in which the nucleus has two nucleoli

Fig. 3. Repr. ⁷⁄₁. Gangl. spin. (Silver-impregnated according to the BIELSCHOWSKY-method with my own modifications) of a six days' old dog. a. Ganglion cell dividing amitotically. b Ganglion cell with the beginning of amitotic division of the nucleus

Fig. 4. Repr. ⁷⁄₁. Gangl. spin. (Impr. as in fig. 3. of a sixty days' old dog. a Colony of apolar cells. Between the three cells in the middle there are bridges of protoplasm

Fig. 5. Repr. ⁷⁄₁. Gangl. spin. (Fix. and staining as in fig. 1) of a 17 days' old dog. The ganglion cell on the left imitates a mitosis. The mitosis in reality belongs to a capsular cell

Fig. 6. Repr. ⁷⁄₁. Gangl. spin. (Fix. and stain. as in fig. 1) of a 17 days' old dog. The mitoses in the capsular cells or in cells subcapsularly situated, which have a tendency to become ganglion cells(?)

Fig. 7. Repr. ⁷⁄₁. Gangl. spin. (Fix. and stain. as in fig. 1) of a 17 days' old dog. Mitosis in the capsular cell

Fig. 8. Repr. ⁷⁄₁. Gangl. spin. (Fix. and stain. as in fig. 1) of a 17 days' old dog. Mitosis in a very young ganglion cell

Fig. 9. Repr. ⁷⁄₁. Spinal cord (Fix. and stain. as in fig. 1) of a 21 days' old Mus musculus var. albus a Mitosis b Amitosis in a young nerve cell.

Fig. 10. Repr. ⁷⁄₁. Spinal cord (Fix. and stain. as in fig. 1) of a 21 days' old Mus musculus var. albus. Syncytium or plasmodium of young nerve cells.

Fig. 11. Repr. ⁷⁄₁. Spinal cord (Fix. and stain. as in fig. 1) of a 21 days' old Mus musculus var. albus. Mitosis in the nerve cells

Fig. 12. Repr. ⁷⁄₁. Spinal ganglion (Impregn. as in fig. 3) of a 17 days' old dog. Bipolar ganglion cell

Fig. 13. Repr. ⁷⁄₁. Spinal cord (Fix. and stain. as in fig. 1) of a full-grown M. musc. v. alb. An example of fairly frequently occurring indentations on nuclei of nerve cells, in my opinion these indentations have very probably no connection with amitotic division

Fig. 14. Repr. ⁷⁄₁. Spinal cord (Fix. and stain. as in fig. 1) of a ten days' old Mus musculus v. albus. An example of a stage in amitotic(?) division in which the nuclei are quite separated but the protoplasmic body is not quite divided

Fig. 15. Repr. ⁷⁄₁. Spinal cord (Fix. and stain. as fig. 1) of a ten days' old Mus musculus var. albus. Cell plasmodium or syncytium, situated just ventrally of the canalis centralis

Fig. 16. Repr. ⁷⁄₁. Spinal cord (Fix. and stain. as in fig. 1) of a ten days' old Mus musculus v. albus. An example of a cell at an early stage of amitotic division

Fig. 17. Repr. ⁷⁄₁. Spinal cord (as in the preceding figure) An example of direct division of the nucleoli and a somewhat later stage then in the preceding figure of direct division of the cell in its entirety

Fig. 18. Repr. ⁷⁄₁. Same material as in the preceding figure. Young ganglion cells (neuroblasts) engaged in direct division

Fig. 19. Repr. ⁷⁄₁. Same material as in the preceding figure. A cell engaged in direct division

Fig. 20. Repr. ⁷⁄₁. Spinal cord (Fix. and stain. as in fig. 1) of a 24 days' old M. mus. v. alb. A young nerve-cell in a far advanced stage of direct division

Fig. 21. Repr. ⁷⁄₁. Same material as in fig. 16. Young nerve cells from the base of the dorsal horn in a very far advanced direct division into four

Figs. 22, 23 and 24 are probable and figs. 25 and 26 certain figures of growth in the roots of the seventh lumbar nerve in a 17 days' old dog. The material is silver-impregnated according to my modifications of the BIELSCHOWSKY-method

Amitotic division.

Most investigators believe, with FLEMMING, that mitotic cell division is the only way in which a new growth in a healthy body can take place. And it is generally admitted that amitotic cell division occurs only in pathological tissues and, apart from this, only in cells that have a very short life. As has been pointed out above, the nerve cells are generally admitted to have a life equal in length to that of the individual; it is therefore obvious that any idea of an increase in these by amitotic division must be out of the question. And I must myself confess that the idea of the permanence and high position of the neurones among the cells in general has become so deeply rooted through studying handbooks of medicine as well as the majority of special treatises on this subject that it is really difficult to get accustomed to the idea that there may be another possibility for the increase in the nerve-cells than mitotic division. If, however, one comes quite freely, as I did, to the problem of explaining the actually existing increase in the nerve-fibres during the whole post-embryonic development, and finds that this explanation has to be sought in an increase in the number of the neurones and not in a cleavage of the axons — and this at the same time as one finds signs of how a large number of the nerve cells are degenerating and dying away, then of course the new formation of ganglion cells, even after mitoses no longer occur in these regions, must be considerable. There are also in the central nervous system, as will be described in more detail below, appearances that seem to indicate that amitotic division of young cells really takes place there. Observations pointing in this direction have already been made and described in literature, although this information seems to have attracted but little attention.

ROHDE[1]) described in 1896 how ganglion cells in invertebrates increase by amitotic division. R. distinguishes four different types of such a division in these animals. As invertebrates have not been the object of my investigations in this matter, I cannot criticize R's statements, although some of them seem somewhat strange.

PALADINO[2]) (1914) describes amitotic division of cells in the central nervous system of vertebrates. P. states that the neurones degenerate and perish, and in connection with this there is a new development of nerve elements. There are good reasons for believing that this

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[1]) ROHDE, l. c.
[2]) PALADINO, l. c.

development takes place by means of the activity of the ependyma and to a subordinate and limited extent by means of direct division. Where these elements exist they sink down and gradually disappear, sending off a first process, which grows and is lengthened, while others are also developed, so that gradually a multipolar cell arises. "Avant d'arriver à cette différenciation, ces éléments se divisent ça et là par scission directe, qui, ou bien se complète — et alors les nouveaux éléments restent en connexion avec un des prolongements — ou bien ne s'achève pas, et on a alors des formations gemellaires de divers degré. Ces faits peuvent s'observer le long de la moelle épinière d'individus d'âge différent et dans des préparations obtenues avec des séries de sections frontales et avec les divers colorations". PALADINO accompanies his statement with a figure to show how the epithelium-cells (ependyma) are further differentiated and move down into the surrounding tissue. On the other hand it is to be regretted that P. did not add a figure showing a cell engaged in direct division and that he did not give a more detailed description of the amitoses in the central nervous system observed by him.

The more thoroughly I study my preparations from the central nervous system of animals of various post-embryonic ages, the more convinced am I that PALADINO is right in his statements as given above. In these preparations of mine I have found, in a number of places, appearances that indicate, just as clearly as P.'s figure, a movement of cells from the ependyma into the surrounding tissue. These appearances are not, however, found continuously along the whole central canal, but occur scattered here and there — this too agrees with P.'s statements. On the other hand, with regard to figures of direct cell division, I have observed a great many which, in my opinion, are to be interpreted in this way. And as a matter of fact I have obtained series of such appearances which show the different stages of a direct cell division. Notches, indentations and irregularities in shape occur very often in the nuclei of the nerve cells. If, however, such appearances be examined more closely, we shall find in most cases that they cannot be counted as figures of amitotic divisions. Thus figures which may with a great degree of probability be considered as stages of amitotic cell divisions do not occur in such abundance in my preparations of the spinal cord from the above-mentioned animals. Fig. 13 shows a type of these notches, which are very common in the nuclei of ganglion-cells, but which, as far as one can see, have nothing at all to do with amitotic divisions of the cells. Figs. 14 and 15 are cell-plasmodia or syncytia, of which one often sees examples, especially close to the ependyma. The

syncytium in fig. 14 was situated immediately beneath the ependyma, and that in fig. 15 in the dorsal horn of the spinal cord in a young white mouse ten days old. Figures 1b, 2a, 3a, 9b, 10, 14, 15, 16, 17, 18, 19, 20, and 21 are pictures of different stages of young nerve cells engaged in amitotic division. These figures are all drawn from appearances in the spinal cord of a white mouse, the two first from an animal 24 days old and the others from 10 days old animals. In the material from toads and dogs that was investigated, similar appearances to those in the white mouse have been found to about the same extent. Fig. 9b shows one stage of direct cell division which in my opinion is very rare; I myself have only found this single case. Fig. 20 shows the most advanced incision usually seen. Transitional stages between this and complete division of the nuclei occur exceedingly seldom. I obtained a particularly welcome opportunity through Professor BOEKE's great kindness during my visit to Holland last summer — of observing in eelembryos that it really is a fact that the appearance of amitoses is very rare in cases where the daughter-nuclei show only very narrow communicating bridges between each other. It is, as we know, generally recognized that the nuclei in the myogene tissue increase by direct division during a later stage of its differentiation into muscular fibres. Eel-embryos are particularly suitable for the study of this development (GODLEWSKI E. [1]). BOEKE's very fine preparations of these embryos showed in this region numerous nuclei engaged in amitotic division. It is worthy of note that here too, among this mass of nuclei in amitotic division, no stage could be discovered in which the nucleus showed a far advanced incision — and consequently a very small communicating bridge between the two daughter-nuclei. — Accordingly, after studying this material, I was inclined to assume that the last part of the process of division took place rapidly, without any narrow drawn-out communicating bridge between the daughter nuclei being formed. With this in view, it is not strange that I looked upon the appearances that form the basis of fig. 21 with a certain amount of surprise and doubt. Does this figure really show stages of amitotic cell division or are they only artifical products? The preparations were well fixed and as a matter of fact do not support the idea of there being artificial products. The nucleoli show a particularly great generative tendency. If we

[1]) GODLEWSKI, E. Ueber Kernvermehrung in den quergestreiften Muskelfasern der Wirbeltiere, Bull. intern. de l'Academie des Scien. de Cracovie, 1900.

[2]) GODLEWSKI, E. Die Entwicklung des Skelet- und Herzmuskelgewebes der Säugethiere. Arch. f. micr. Anat. B. 60, 1902.

add that this picture is the only one among my extensive material in which I found such far advanced incisions in the nuclei, these facts certainly support the idea that there really are natural formations. All these cells that show signs of amitotic division are very young. Some of them have no signs at all of processes (fig. 19 and 20), while others show indications of the beginning of a development of these (figs. 9b, 16, 17, 18, and 21). I can agree with PALADINO's statement quoted above that it is only before the differentiation of the processes that amitotic division takes place. On the strength of the appearances in this material I am of the opinion that the amitotic division proceeds in the way:

a) The nucleolus [1]) increases in length and begins to show incisions in the middle; this incision becomes deeper and deeper (figs 16 and 17) and finally we have a division into two nucleoli, each of which moves to an end of the nucleus of the cell, which has begun to become drawn out into a more or less oval formation. The nucleoli often exhibit a continued power of generation even after they have moved out to the future daughter-nuclei; it is this that causes us often to see in such daughter-nuclei either one nucleolus engaged in direct division or else several nuclei, a number of which may be seen moving out of the nucleus. I have not been able to decide with certainty whether the filaments (nuclear fibres) of the nucleus thereby have any specific function. It is a fact, however, that there are sometimes appearances which point to this being really the case (fig. 16 and 17). b) The drawn-out, elliptical nucleus begins to show signs of incision in the middle (fig. 16, 17, and 18). This incision usually takes place in the middle, so that the two daughter-nuclei are equally large. There are, however‘ figures showing the existence of a slight dissymmetry (fig. 18). The incision grows deeper, but is not as a rule, however, deeper than is shown in fig. 20, the connection between the nuclei being retained. Incision of the nuclei as far advanced as that shown in figs. 9b and 21 is exceedingly infrequent and these figures are the only ones I found of this type. There are also figures that indicate that the fibres of the nucleus may have something to do with the division of the nucleus. c) If the cell in which the nucleus divides amitotically is at a very early stage of development, a cleavage of the protoplasm does not, in most cases, ensue, but a cell plasmodium arises. These cells are

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[1]) It should, however, be noted that such phenomena of new growth often appear in the nucleoli without the nucleus otherwise showing any signs of an amitotic division.

then situated most frequently in the neigbourhood of the central canal (fig. 15). If the cell is at a somewhat later stage of development, an incision of the nucleus is usually accompanied by a division of the surrounding protoplasm, which even at the same stage shows protoplasmic processes engaged in development (fig. 10). Cells of this last type are situated farther away from the central canal.

It is noteworthy that the structure of the nucleus in the cell engaged in amitotic division seems to be relatively intact in comparison with the corresponding condition in mitotic cell division.

With regard to the degree of the neurone formation I think that, on the ground of the reasons given above, I may go a step further than Paladino when he writes: "En conclusion, le tissu nerveux ne fait pas exception à la loi, d'après laquelle tout tissu vit dans l'ensemble et se renouvelle isolément, pour remplacer les éléments qui se détériorent et se détruisent; en d'autres termes, le tissu nerveux, lui aussi, est un siège de *regénération* pour ainsi dire *restauratrice.*" It seems to follow from what has been shown above that we are not dealing with merely a restoration of, but also with an increase in the number of neurones.

In order to complete this survey I shall add the results of my investigations of the

Appearances of growth

of the axons in the dorsal and ventral roots of the spinal nerves. As has already been shown above, the calculations of the number of the nerve fibres in cross-sections of the dorsal and ventral roots of the spinal nerves made at a, a_1 and b, b_1 text fig. 1 gave such values that one might expect that figures of growth might also really be shown in longitudinal sections of these roots. Silver-impregnated roots from some intact lumbal nerves of a 17 days old dog were set up in series of sections of suitable thickness, and then the preparations were searched for figures of growth. These investigations showed the occurrence of a large number of figures of nerve-fibres free from medullary sheaths, whose ends are situated between the two section surfaces of the preparations; the shape of these ends shows that they could scarcely be due to the nerve-fibres having been cut off when the sections were cut. Of the different shapes that the ends of these nerve-fibres take I will only mention one here, namely, that which shows a swelling at the point; this swelling has in most cases a claviform shape (figs. 22, 23, 24, 25, and 26). The nerve-fibres in these cases were very fine, and showed repeated convolutions during their course (fig. 26). A large number of such nerve-

fibres with a winding course were to be found in my preparations, although I could not find the free end of all of them. Of these figures of growth at least those that form the basis of figs. **22, 25,** and **26** may be considered as being absolutely reliable. These figures resemble, of course, those usually found in preparations of nerves engaged in regeneration (in the regeneration of a peripheral end of a nerve, being produced experimentally), BOEKE, RAMON Y CAJAL, etc. We thus arrive at the interesting fact that in the roots of the segmental nerves of fully intact animals as old as those we are dealing with there really exist neurites engaged in growth, and also a new formation of neurones — a phenomenon that must be considered of fundamental importance for a comprehension of the post-embryonal growth of the whole individual.

Résumé and conclusions.

The investigations of the material in question have shown that the post-embryonic growth of the peripheral nerves is not due — as far as the axons are concerned — solely to an advancing myelinisation (DONALDSON, etc.) and an increase in the thickness of the separate axons, but is also due to an increase in the number of axons. This increase in the number of axons is, however, relatively larger during the earlier than during the later post-embryonic period of the animal's development. It is of special interest to note that the results of counting the axons show that the increase in the number of axons goes on for a considerable length of time during the post-embryonic life of the individual (see the table). This post-embryonic period during which an increase in the number of nerve fibres in the roots of the spinal nerves takes place is many times longer than that during which mitoses can be shown in the spinal ganglia and the spinal cord.

Investigations carried out with the object of explaining the method in which such a post-embryonal increase in the number of axons arises have shown that it can *not* be explained by means of T- or Y-division of the nerve fibres or by assuming that the same nerve cell sends off more than one axon, but that the explanation must be sought *in a real increase in the number of the neurones.* This increase in the neurones seems to a great extent to be due to the fact that from young cells lying in reserve processes are developed, among which the so-called axons grow out in, among other regions, the roots of the nerves and the peripheral nerves. Probably the young cell material in the spinal cord comes from undifferentiated

cells in the ependyma and that in the spinal ganglia from undifferentiated cells among the capsular cells. These cells increase during their differentiation into ganglion cells, among others, partly by means of mitotic division and as far as I can see from my preparations also partly by means of amitotic division. This post-embryonic increase in the number of the cell-material is greater during the first month of post-embryonic life, but seems to continue afterwards as well. It is only during the first month of the post-embryonal life of the individual that one sees mitoses in these cells, but even during its continued life cell-division seems to occur; it then takes place amitotically. These new ganglion cells that have arisen by mitotic or amitotic division seem to develop into neurones, which not only replace older neurones that have been destroyed by degeneration (PALADINO), but also help to increase the absolute number of neurones.

Figures of growth for the axons have been shown morphologically in the dorsal and ventral roots of the lumbar nerves of a 17 days old dog [1]. These figures of growth have been, among various other shapes, claviform — thus under completely physiological conditions the same shape is found for the figures of growth of the axons as is usually found in experimentally produced regeneration of peripheral nerves.

Addendum.

It seems as if the post-embryonal increase in the neurones can be effected by external influences. Thus, for instance, it has appeared that in growing animals (among others *Mus musculus var. albus*) the increase in the number of axons can be intensified by suitably adapted and gradually increased training. If, on the other hand, the training has been made too intense, quite a contrary result is obtained — the number of axons has been found to be relatively less in these animals than in the controlling animals. During my continued investigations of this problem I have succeeded in showing, in, among other animals, a 3,5 year old dog, numerous transitional stages from indifferent cells — as large as small capsular cells — to fully developed ganglion cells. These different transitional stages have been examined with regard to the position, size, offshoots and neuro-fibrillar structure of the cells. These questions will be dealt with more fully in a later and more complete account.

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[1] This is the oldest animal that I have investigated so far with regard to this.

Chemistry. — *"Catalysis.* (Part VI). *Temperature coefficients of heterogeneous reactions."* By Nil Ratan Dhar. (Communicated by Prof. Ernst Cohen).

(Communicated in the meeting of February 22, 1919).

In foregoing papers [1]), the temperature coefficients of catalysed and uncatalysed reactions in a homogeneous medium have been studied. It has been shown that a positive catalyst produces a lowering in the value of the temperature coefficient of the reaction, the reverse is the case with a negative catalyst. It was also proved that the higher the order of a reaction, the smaller is the temperature coefficient.

The object of this paper is to discuss the experimental researches and find, if possible, similar relations in the domain of heterogeneous reactions.

In order to make clear the question of the temperature coefficients of heterogeneous reactions, it is necessary to indicate briefly their characteristics.

In a reaction between a liquid and a solid, according to the diffusion theory of reaction velocity a thin layer of liquid adhering to the solid remains unaffected by stirring and the reaction is maintained by the transport of dissolved substances across this layer of diffusion. Moreover, it is assumed that at the boundary surface between two phases, the velocity of the chemical reaction is extremely high. When the diffusion is sufficiently slow compared with the other stages of the reaction the velocity of the whole reaction will be determined by the rate of diffusion alone.

This theory was first proposed by Noyes and Whitney [2]) for some special cases, but its general applicability to various types of heterogeneous reactions was indicated by Nernst and Brunner [3]), and has since been accepted by several investigators as giving the best explanation of facts in heterogeneous systems.

On the other hand, the general applicability of the diffusion theory

[1]) Jour. chem. soc. 1917, **111**, 707; Annales de chimie, 1919.

[2]) Zeit. Phys. Chem. 1897, **23**, 689.

[3]) ibid. 1904, **47**, 52, 56.

was contested by Ericson-Auren and Palmaer[1]), Tammann[2]), Marc[3]),
Senter[4]), Wildermann[5]) etc.

Since, according to the diffusion theory, in chemical reactions
which occur merely at the boundary between two phases, the
phenomenon is essentially one of diffusion, it is useless to try and
determine the order of reactions from the rate at which they proceed;
this method of argument is only applicable, according to kinetic
considerations to the probablity of collisions in homogeneous systems
and loses its significance when applied to heterogeneous systems.
Moreover, if the velocity is controlled by a diffusion process, one
will get a coefficient of the velocity similar to that for a uni-molecular
reaction and the coefficient will be independent of the actual order
of the more rapid chemical reaction, which accompanies the process.
Consequently it is impossible to establish a relation between the order
of a reaction and its temperature coefficient in heterogeneous systems.

(a)   Temperature coefficients of uncatalysed reactions.

Another consequence of the diffusion theory is that the tempera-
ture coefficient for an elevation of $10°$ should be of the order 1.3 i.e.
of the same order of magnitude as the temperature coefficient of
diffusion (compare Ohölm[6])). We shall now see if experimental
results confirm this inference from the diffusion theory. The following
is the summary of results. (See table 1 next page).

These results support the diffusion theory of reaction velocity in
heterogeneous medium. In this connection it is interesting to observe
that elevation of temperature up to a certain limit is found to be
without influence on the decomposition of some alcoholic compounds
by sodium amalgam (Löwenherz, Zeit. Phys. Chem. 1900, **32**, 480;
1902, **40**, 400) and on the velocity of dissolution of Casein in
alkalies (Robertson, Jour. Phys. chem. 1910, **14**, 377).

On the other hand, the following summary of results shows that
the conclusion as to the effect of temperature, is not corroborated
in these cases. (See table 2 next page).

It has already been pointed out that velocities of diffusion only
determine the rate of reaction when no other processes interfere
and specially when no slow processes, taking place in the homogen-

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[1]) Zeit. Phys Chem. 1906, **56**, 689.
[2]) ibid. 1910, **69**, 257.
[3]) ibid. 1908, **61**, 385; 1909, **67**, 470.
[4]) Jour. Phys. Chem. 1905, **9**, 311.
[5]) Zeit. Phys. Chem. 1909, **66**, 445.
[6]) ibid. 1905, **50**, 309; 1910, **70**, 385.

TABLE 1.

Reaction.	Reference.	$\dfrac{k_{t+10}}{k_t}$
(1) $CaCO_3 + HCl$	SPRING (Zeit. Phys. Chem., 1887, **1**, 209)	1.5
(2) Metals + acids	VELEY (Journ. chem. soc. 1889, **55**, 361)	1.21
(3) „	ERICSON-AUREN(Zeit.anorg.Chem.1901,**27**,209)	1.1
(4) Solution of $CaSO_4 . 2 H_2O$ in water	BRUNER and TOLLOCZKO (Zeit. Phys. Chem. 1900, **35**, 283)	1.5
(5) Various reactions	BRUNNER (Zeit. Phys. Chem. 1904, **47**, 56)	1.3
(6) Evaporation of water	JABLCZYNSKI(Jour. chim. Phys. 1912,**10**, 241)	1.1
(7) Cu and NH_4OH	YAMASAKI (7th Inter. Cong. App. Chem. 1909, Sec. X, 172)	1.15
(8) O_2 and pyrogallates O_2 and haemaglobin CO and „	BOSELLI (J. Chim. Phys. 1911, **9**, 689; 1912, **10**, 1)	1.1
(9) Halogens and metals Chromic acid and metals Ferric salts and metals	VAN NAME and his associates (Amer. J. Science 1910 [4], 237; 1916 [4], **42**, 301; 1917 [4] **43**, 449)	1.28
(10) Quinol and O_2	EULER and BOLIN (Zeit. Physiol. Chem.1908, **57**, 80)	1.2
(11) Dissolution of various salts in water	WAGNER (Zeit. Phys. Chem. 1910, **71**, 401)	about 1.2
(12) Dissolution of CO_2 and O_2 in water	CARLSON (Medd. K. Nobel Inst. bd **2**, N[0]. 5, 1910).	1.4
(13) Mg and HCl	BONSDORFF (ibid bd. **3**, N[0]. 8, 1915)	1.44

TABLE 2.

Reaction.	Reference.	$\dfrac{k_{t+10}}{k_t}$
(1) Dissolution of benzoic acid in water	BRUNER and TOLLOCZKO (loc. cit.) WILDERMANN (loc. cit.)	1.8
(2) Ni and CO	MITTASCH (Zeit. Phys. Chem. 1902, **40**, 1)	1.53
(3) Development of photographic plates	SHEPPARD and MEES (Proc. Roy. Soc. 1905, **76**, 217)	2.
(4) Precipitation of AgCl, AgBr etc.	JABLCZYNSKI (Zeit. Phys. Chem. 1913, **82**, 115)	2
(5) Slow oxidation of S	BODENSTEIN and KARO (ibid. 1911, **75**, 30)	1.87
(6) H_2 and $KMnO_4$ CO and $KMnO_4$	JUST and KAUKO (ibid. 1911, **76**, 601; 1913, **82**, 71)	2.
(7) Velocity of absorption reversal of (a) HgS (b) S	FREUNDLICH and associates (ibid. 1913, **85**, 660; 1915, **89**, 147)	(a) 4 (b) 5
(8) Ferrous salts and oxygen	Mc. BAIN (Journ. Phys. Chem. 1901, **5**, 623) BOSELLI (loc. cit.)	2.2

eous phase is connected with the progress of the reaction. It seems probable, that in the examples of reactions cited in Table 2, the changes concerned are *real* chemical reactions rather than diffusion processes. For these reactions it would be interesting to find out a relation between their orders and their temperature coefficients, but unfortunately no experimental work in this direction is available.

(b) *Temperature coefficients of catalysed reactions.*

We shall now consider the temperature coefficients of reactions catalysed heterogeneously. The following is the summary of important reactions investigated up till now:

TABLE 3.

Reaction.	Reference.	$\dfrac{k_{t+10}}{k_t}$
(1) Decomposition of H_2O_2 by catalase (blood)	SENTER, Zeit. Phys. Chem. 1903, **44**, 257	1.7
(2) Decomposition of H_2O_2 by colloidal Au, Pt, Ir etc.	BREDIG and his pupils, ibid 1899, **31**, 258, 320; 1901, **37**, 1, 323; 1901, 38, 122; 1909, **66**, 175	1.6
(3) Decomposition of H_2O_2 by colloidal Ag	MC. INTOSH, Jour. Phys. Chem. 1902, **6**, 15	5
(4) Decomposition of H_2O_2 by colloidal MnO_2	MARK. DISSERT. Heidelberg 1907	2
(5) Hydrogenation in presence of colloidal Pd	ZALKIND and PITCHTSCHIKOFF, J. Russ. Phys. Chem. Soc. 1914, **46**, 1527	1.75
(6) Oxydation of NaH_2PO_2 by colloidal Pd or Pd black	SIEVERTS and PETERS, Zeit. Phys. Chem. 1916, **91**, 199	2
(7) Reduction of methylene blue by H.COOH in presence of colloidal metals	BREDIG and SOMMER, ibid 1910, **70**, 34	2
(8) Decomposition of (*a*) H.COOH and (*b*) H.COONa in presence of colloidal Rh	BLACKADDER, ibid 1913, **81**, 385	(*a*) 2 (*b*) 2.5
(9) Oxydation of phenyl thiocarbamide in presence of blood charcoal	FREUNDLICH and BJERCKE, ibid 1916, **91**, 1	2.3
(10) Oxydation of oxalic acid in presence of blood charcoal	WARBURG, Pflüg. Arch. 1914, **155**, 547	2.1
(11) Enzyme actions	Generally higher than	2

The following table shows the summary of results obtained with catalysts in the solid state:

TABLE 4.

Reaction.	Reference.	$\dfrac{k_t + 10}{k_t}$
(1) Decomposition of ozone	PERMAN and GREAVES (Proc. Roy. Soc. 1908, **80** A, 353)	about 1.2
(2) $SO_2 + O \rightarrow SO_3$	BODENSTEIN and his pupils (Zeit. Phys. Chem. 1903, **46**, 725; 1905, **53**, 166; 1907, **60**, 1, 46; 1911, **75**, 30; 1912, **80**, 148; Zeit. Elektrochem. 1905, **11**, 373; Festschrift W. NERNST, 1912, p. 99.	1.36
(3) $CO + O \rightarrow CO_2$		1.40
(4) $SO_3 \rightarrow SO_2 + O$		1.57
(5) $NH_3 \rightarrow N + 3H$		1.10
(6) $H_2 - O \rightarrow H_2O$		1.18
(7) Decomposition of H_2O_2	BREDIGAND TELETOFF (Zeit. Elektrochem 1906, **12**, 581)	1.28
(8) $Cr^{\cdots} + H^{\cdot} \rightarrow Cr^{\cdots} + H$	JABLCZYNSKI (Zeit. Phys. Chem. 1908, 64, 748)	1.29
(9) $Ti^{\cdots} + H^{\cdot} \rightarrow Ti^{\cdots} + H$	DENHAM (ibid 1910, **72**, 641)	1.29

It will be seen at once on glancing at the two foregoing tables that in the reactions catalysed by solids (with the exception of blood charcoal) the temperature coefficient is about 1.3 i.e. of the same order as that for diffusion; whilst in the case of reactions catalysed by colloidal metals and enzymes the temperature coefficient is about 2 i.e. of the same order as that of an ordinary chemical reaction in homogeneous medium. How is this difference to be explained? With catalysts, which cause reaction between the substances in question to take place with practically infinite velocity, the actual rate of reaction will be determined solely by the velocity with which the reacting substances diffuse to the surface of the catalyst; whether such a catalyst exists, must of course be determined separately for every case.

Adsorption is now considered to be an exceedingly rapid process. If the reacting substances were brought to the surface of the catalyst by capillary forces, the temperature coefficient would correspond to that of the slower process, namely, the chemical change involved. If, on the other hand, the reacting substances are brought to the surface by the slow process of diffusion, then the measured velocity would be that of a diffusion process and the temperature coefficient would be of the order of 1.3, which we have seen in the case when solid catalysts are used. To account for the high temperature coefficient in the case of reactions catalysed by colloidal substances and enzymes, one might suppose that the Brownian movement of these particles acted as very efficient stirring in such a way that the diffusion layer was removed as fast as it was formed, with the

result that the homogeneous chemical reaction in the adsorbed layer is the real process of which we determine the temperature coefficient.

Now it is interesting to observe that BREDIG and TELETOFF (Zeit. Elektrochem. 1906, **12**, 583) have calculated the thickness of the diffusion layer from the NERNST diffusion expression (Zeit. Phys. Chem. 1888, **2**, 634), utilising the data obtained from the decomposition of hydrogen peroxide in presence of colloidal platinum and found the thickness to be 0.05 mm. i.e. of the same order as BRUNNER found in the case of the dissolution of benzoic acid in water. This seems to show that in spite of the Brownian movement the diffusion layer remains unchanged. If this is true, the above explanation of the high temperature coefficient in the case of colloids and enzymes breaks down. Moreover, on this point of view, the high values of the temperature coefficient obtained in the oxidations of oxalic acid and phenylthiocarbamide in presence of the solid catalyst blood-charcoal, remain entirely unexplained.

Looking at the whole problem, it seems probable that in some cases the slow chemical change affects the velocity of the total reaction, whilst in other cases, diffusion plays the most important role and it is desirable to investigate fully the kinetics of each individual case.

Certainly much light would be thrown on the whole question if we can study the kinetics and temperature coefficients of one and the same reaction without any catalyst and in presence of both homogeneous and heterogeneous catalysts. The velocity of decomposition of hydrogen peroxide, for example, may be investigated at various temperatures (1) without any catalyst and (2) in presence of iodides or any other substance soluble in water (compare BREDIG and WALTON. Zeit. Phys. Chem. 1904, **47**, 185) and (3) in presence of colloidal metals, MnO_2, charcoal, solid metals etc.

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Chemistry. — "*The heterocinnamic acids of* Erlenmeijer Jr." By
A. W. K. de Jong, corresponding member at Buitenzorg.
(Communicated by Prof. P. van Romburgh.)

Besides the storax cinnamic acids there are, according to Erlen-
meyer Jr., two other normal cinnamic acids, the heterocinnamic
acids, which were separated from synthetic cinnamic acid.

Erlenmeyer asserts that the difference between storax- and hetero-
cinnamic acid consists solely in the different mode of crystallisation
of these acids from ether. He says:[1] "Wie ich schon in der ersten
Abhandlung erwähnt habe, steht bei der Bearbeitung der Zimtsäuren
als einziges brauchbares Unterscheidungsmerkmal die verschiedene
Krystallisationsart der Storaxzimtsäure und der synthetischen Zimtsäure
aus Aether zur Verfügung. Mit Hilfe dieses allerdings ungewöhnlichen
Unterscheidungsmittels gelang es, zu zeigen, dass die synthetische
Zimtsäure nach verschiedenen mitgeteilten Methoden in zwei unter
einander und von der synthetischen Säure verschiedene Säuren, die
Storaxsäure und die Heterosäure, zerlegt werden kann, welche bei
der Analyse einen Unterschied in der Zusammensetzung nicht erkennen
liessen," while on page 502, loc. cit., he writes: "Begnügt man sich
damit, beide Säuren aus Wasser zu krystallisieren und die Schmelz-
punkte zu bestimmen, so wird man keinen so wesentlichen Unterschied
wahrnehmen, dass die Annahme einer prinzipiellen Verschiedenheit
berechtigt erschiene. Ganz anders aber, wenn man die beiden Säuren
in Aether löst und diese Lösungen langsam verdunsten lässt. Aus
der aetherischen Lösung der Storaxsäure erhält man so ohne Mühe
wasserklare, dicktaflige, gut ausgebildete Krystalle, welche mehrere
Zentimeter gross und über 2 mm. dick werden können; aus der
aetherischen Lösung der reinen synthetischen Zimtsäure dagegen
krystallisieren unter genau den gleichen Bedingungen Aggregate von
über einander geschichteten, mit einander verwachsenen, äusserst
dünnen Lamellen, welche meist keine geradlinigen Umgrenzungslinien
erkennen lassen." "An demselben Thermometer beobachtet, schmilzt

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[1] Ber. **42**, 2649.

die synthetische Säure bei 132—133°, die Storaxsäure bei 134—135°.[1])"

It was shown by Ruber and Goldschmidt[2]) that the differences between the synthetic and storaxcinnamic acid observed by Erlenmeyer, can easily be attributed to impurities in the synthetic acid, since the mode of crystallisation of cinnamic acid is strongly influenced by traces of other acids such as chlor- or nitro-cinnamic acids. They found that commercial synthetic cinnamic acid contained chlor-cinnamic acid as an impurity.

To this Erlenmeyer[3]) answered that even synthetic cinnamic acid prepared from pure, well crystallised storaxcinnamic acid by dissolving in alkali, oxidising with permanganate to benzaldehyde, and then from this preparing the acid by the Perkin synthesis, exhibits the same peculiar crystalline form.

In spite of this answer, a study of Erlenmeyer's papers leads to the conclusion that heterocinnamic acid is not a pure substance, and that the difference from ordinary cinnamic acid found by him must be referred to some impurity.

According to Erlenmeyer[4]) both synthetic and heterocinnamic acids can be transformed, although with a 10°/₀ loss, into storaxcinnamic acid by heating their colourless aqueous solutions with animal charcoal. Also repeated sublimation[5]) brings about the transformation of heterocinnamic into storaxcinnamic acid. He also succeeded by fractional precipitation[6]) of the sodium salt of synthetic cinnamic acid in easily separating 90 °/₀ as storaxcinnamic acid, whereas synthetic cinnamic acid should consist of storaxcinnamic acid to the amount of 50 °/₀.[7]) He says then:[8])

"Da die Heterozimtsäure, trotz der Gewinnung von Storaxzimt-säure aus ihr, in ihren Eigenschaften unverändert bleibt, kann man nicht anders annehmen, als dass bei dem fortgesetzten Fraktionier-ungsverfahren ein allmählicher Uebergang von Hetero- in Storax-zimtsäure stattfindet".

In his detailed papers no indication is given of the method which he used for the preparation of pure cinnamic acid for his investi-

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[1]) Further particulars of the crystalline forms are given in Biochem. Zeitschr. **34**, 366 and in Ber. **42**, 507.

[2]) Ber. **43**, 453.

[3]) Ber. **43**, 955.

[4]) Ber. **43**, 1076.

[5]) Ber. **42**, 2658.

[6]) Bioch. Zeitschr. **34**, 423.

[7]) Bioch. Zeitschr. **34**, 425.

[8]) Ibidem 424.

gations. Evidently he assumes that well crystallised storaxcinnamic acid [1]) can contain not even minimal amounts of impurities. Here, however, it is a question of traces of impurity, seeing that so small a quantity as 1 % of p-chlorocinnamic acid can so influence the crystallisation of storaxcinnamic acid that it shows a perfect resemblance to the synthetic acid, [2]) while only 0.3 % of o-nitrocinnamic acid was necessary to produce the same effect. [3]) If the impurity occurs in smaller amount, it is possible that its effect on the crystalline form is not observed. The reason why ERLENMEYER was always able to prepare so-called synthetic cinnamic acid from cinnamic acid derived from various sources must thus be looked for in the impurity of the materials used. Whether or not this impurity was the same in all cases may for the present be left out of consideration. It must, however, have been a substance which on oxidation gives an aldehyde from which by the PERKIN reaction a substituted cinnamic acid is formed. In the oxidation with permanganate the benzaldehyde has relatively the better chance of being oxidised to benzoic acid than the aldehyde impurity, which occurs only in traces, since, the vapour present being generally unsaturated with respect to the latter, the impurity is more quickly removed from the liquid reaction mixture. The amount of the impurity in the benzaldehyde will thus be greater than in the cinnamic acid originally used. In the PERKIN synthesis, according to the researches of ERLENMEYER himself, the aldehyde impurity is more completely transformed into the substituted cinnamic acid than the benzaldehyde, since the cinnamic acid obtained was the so-called synthetic acid, while fine crystals of storaxcinnamic acid were deposited from the residual benzaldehyde. The cumulative result of these circumstances should be that the amount of the impurity is increased, and its effect in modifying the crystalline form rendered perceptible.

It seemed to me thus necessary to ascertain whether synthetic cinnamic acid can in fact be prepared from pure cinnamic acid in the way indicated by ERLENMEYER, and if the product has the properties observed by him.

Preparation of pure cinnamic acid.

As raw material the ethereal oil extracted from the roots of Alpinia malaccensis was used. This consists, according to the researches

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[1]) Ber. **43**, 957. He speaks here of "25 gr. der als einheitlich anerkannten Storaxzimtsäure".

[2]) RIIBER and GOLDSCHMIDT Ber. **43**, 460 and Biochem. Zeitschr. **34**, 406.

[3]) Ber. **43**, 461.

of van Romburgh,[1]) mostly of the methyl ester of cinnamic acid. Erlenmeyer[2]) states that on treatment with ether the cinnamic acid prepared from Alpinia gave crystals on the sides of the beaker which resembled the synthetic acid, while on the bottom beautiful crystals of a-storaxcinnamic acid were formed.

The ethereal oil was saponified, the solution extracted three times with light petroleum, and the acid precipitated, filtered, and washed. On oxidation with potassium permanganate the mixture foamed up vigorously so that the distillation had to be continually interrupted in order to avoid frothing over, although the flask was sufficiently large. For this reason the yield was very poor. In order to purify it, the acid was therefore dissolved by heating in sodium carbonate solution. On cooling the solution was extracted three times with light petroleum, and the acid again precipitated. This product gave no frothing on oxidation with potassium permanganate. Cinnamic acid prepared by the Perkin synthesis separates out, according to Erlenmeyer[3]), after treatment with ether in characteristically developed crystals of a-cinnamic acid, which exhibited no perceptible difference from the original acid.

The cinnamic acid was then dissolved in caustic soda solution in just sufficient quantity of the latter, so that 1 gr. of the 9 gr. acid present remained unneutralised[4]). The solution was then well boiled, and the acid separated completely by shaking after cooling. From solution in ether the acid crystallised in large flat plates which differed from the original acid in their size and thinness. Hetero-cinnamic acid, which, according to Erlenmeyer, should result from this procedure, was not obtained. The crystals did not correspond with those of the so-called synthetic cinnamic acid, since the edges were straight and the angles well formed. They approximated closely to them, however, and showed also iridescence.

The possibility was not excluded that the difference from the naturally occurring acid was due to an impurity in the cinnamic acid used. For this reason I have subjected the substance to different processes of purification, which may be briefly indicated in the following.

Purification of the methylester by crystallisation.

For this purpose more than 5 kilos of the ethereal oil were taken

[1]) These Proceedings, April 1898.

[2]) Ber. **39**, 1581.

[3]) Biochem. Zeitschr. **34**, 406. In place of beakers Erlenmeyer used flasks.

[4]) Ber. **42**, 519.

from which, merely by allowing to stand, a large portion of the
ester separated out in crystals. It was purified by melting and by
allowing it to recrystallise slowly at the prevailing temperature
(about 25—30°). The portion which still remained liquid after 24
hours was removed by draining. This procedure was repeated until
the ester solidified entirely within 24 hours. Its melting point mea-
sured on an Anschütz thermometer placed in the substance was
34° (a trace of water was present).

From 28 gr. of this ester a yield of 7.7. gr. of benzaldehyde was
obtained, which gave 4.25 gr. of cinnamic acid, while more than
3 gr. of benzaldehyde were separated which had not taken part in
the reaction [1]). Only 17°/₀ of the quantity of cinnamic acid used is
thus recovered as synthetic product. The synthetic acid was recrys-
tallised from boiling water to free it from a small amount of brown
impurity. On treatment with ether well developed crystals of α-cin-
namic acid were obtained with straight edges and sharp angles.
The product, like the acid previously obtained, showed none of the
properties which ERLENMEYER ascribes to the so-called synthetic
cinnamic acid.

16 gr. of synthetic product were then prepared from the ester
by ERLENMEYER's method, and from this 1 gr. was separated by
dissolving in an insufficient quantity of a boiling solution of caustic
soda. This last product crystallized from ether in thin transparent
superposed glittering plates showing iridescence. Of these several had
curved edges. From benzene solution large thin plates with partly
curved edges separated out which under the influence of light gave
α-truxillic acid. On cooling the hot petrol solution locally small
curved needles were obtained, which on exposure to light were trans-
formed into β-truxillic acid. The properties of the first portion agree
with those of synthetic cinnamic acid as given by ERLENMEYER,
whereas, according to the method of preparation, heterocinnamic
acid should have resulted.

That in this case so-called synthetic cinnamic acid was obtained,
while the original oil treated in the same way gave a product in
which these properties were not yet fully developed, must probably
be attributed to the quantities of the cinnamic acid used, 9 gr. and
16 gr., from which the first fractions were prepared.

It may also be pointed out that so-called synthetic cinnamic acid
apparently occurs in two forms, an α- and a β-form. This fact is
not mentioned by ERLENMEYER.

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[1]) These figures are the means of eight preparations.

A further purification of the ester by crystallisation was undertaken. A large vessel full of water was placed in a hay box. When the ester was placed in the water its temperature was 36° and after 24 hours, 32°. After repeated crystallisations the melting point of the ester was 34°.8—34°.9. The determination was made by heating the ester in a testtube provided with an air-jacket in a bath at 45°. A thermometer reading to $\frac{1}{20}$ of a degree was placed in the substance, and the readings plotted on a curve.

The following temperatures are given as the melting-point of this ester: 33°[1]), 36°[2]) near 36°[3]), 34°[4]), while SCHIMMEL and Co. found 36° for the ester from Wartara-oil, and 34° -35° for their own preparations[5]). From this ester 16.5 gr. synthetic cinnamic acid was prepared according to ERLENMEYER. The first portion separated from the solution of the sodium salt; about 1 gr., was found on testing with ether to be ERLENMEYER's synthetic cinnamic acid.

Purification of cinnamic acid by crystallisation from water.

200 gr. cinnamic acid prepared from the roots of Alpinia Malaccensis, was dissolved by boiling in about 16 litres of water. On the following day the crystallised acid was filtered off and again dissolved in 16 litres of water. This procedure was repeated ten times. The quantity of cinnamic acid had then been reduced to about 40 gr. 20 gr. of this product was then recrystallised four times from water and from the final product synthetic cinnamic acid was prepared by the method indicated by ERLENMEYER.

From 17 gr. of the synthetic acid the first fraction, about 1 gr., was separated and was deposited from ether in well formed thin plates of cinnamic acid. These were larger and thinner than those given by the original acid and were to some extent superposed. Curved edges were not shown. The substance was thus not identical with so-called synthetic cinnamic acid according to ERLENMEYER.

Purification of cinnamic acid by crystallisation from 96 % alcohol.

860 gr. cinnamic acid, separated from the ethereal oil was dissolved in 1720 c.c. hot alcohol, and after filtration the solution was made to crystallise by cooling and stirring. In this way a mass of

[1]) ANSCHÜTZ and KINNICUTT, Ber. 11, 1220.

[2]) WEGER, Ann. 221, 74.

[3]) VAN ROMBURGH, l. c.

[4]) ULTÉE, Mededeeling v. h. Alg. Proefstation at Salatiga II, N⁰. 45.

[5]) GILDEMEISTER and HOFFMANN, Die aeth. Oele, 2e Aufl. I, 522.

very small crystals was obtained, which, when filtered off and washed with alcohol, gave 241 gr. of cinnamic acid. The product was recrystallized once more in the same way. The synthetic acid prepared from this gave a first fraction of 1 gr. from 13.5 gr., which was unmistakably ERLENMEYER's so-called synthetic acid.

It appears therefore from this investigation that the heterocinnamic acids of ERLENMEYER JR. are not obtained by the method described by him from pure cinnamic acid. Their formation is to be ascribed to an impurity in the cinnamic acid which he used.

The heterocinnamic acids are therefore not pure chemical compounds.

A remark on the reaction of BEILSTEIN may be made here. ERLENMEYER makes the following statement: [1] "Es mag hier darauf hingewiesen werden, dass selbst die best krystallisierte Storaxzimtsäure, welche bei der Prüfung mit Soda und Salpeter sich chlorfrei erweist, mit der Kupferoxydperle in der Flamme des Bunsen-Brenners erhitzt, dieser eine intensiv grüne Färbung zu verleihen vermag."

I have also found that cinnamic acid, by whatever method it was purified, always gave BEILSTEIN's reaction, although only faintly.

The methylester, even the unpurified substance, gave no coloured flame reaction when heated with copper oxide. The copper salt is, however, quickly formed by heating cinnamic acid and copperoxide, and the same salt, prepared from an alkaline solution of the ammonium salt by precipitation with copper sulphate, gave the reaction more distinctly than the free acid.

According to ERLENMEYER Jr., pure copper carbonate also gives the reaction. Possibly the BEILSTEIN reaction is more sensitive for acids than for neutral substances or altogether inapplicable in the case of most acids. In the meantime no conclusion can be arrived at since the possibility of the presence of impurity, even in small quantity, in the cinnamic acid used by me is not excluded.

Buitenzorg, August 1918.

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[1] Ber. **43**, 956 note.

Chemistry. — *"On Metastable Unmixing and the Classification of Binary Systems."* By Prof. F. E. C. Scheffer. (Communicated by Prof. Böeseken).

(Communicated in the meeting of January 25, 1919).

1. In the recently published work on systems with two liquid phases Büchner discusses in § 4 the different spacial figures of systems in which besides two liquid layers there also occur compounds. [1]) He successively discusses there the systems with quadruple points $VL_1 L_2 G$ (V = compound), and those which present analogy in behaviour with the system diphenylamine-carbonic acid, which was closely examined by Büchner.

In my recently published paper on the phenyl- and tolyl-carbaminic acids[2]) I have pointed out that the systems aniline, resp. toluidine-carbonic acid belong to the category first discussed by Büchner, and that with a suitable choice of the homologues of aniline a transition can appear in the second case discussed by Büchner. The latter I have, however, indicated as the type sulphuretted hydrogen-ammoniac. In reference to this the following remarks may be made.

2. In all the systems in which a three phase line SLG intersects the critical line part of the latter is not stable, and if retardations are not possible, it is, therefore, not realizable. This not realizable part of the critical line can be either entirely metastable, or partly metastable, partly unstable. Neither possibility can be demonstrated directly experimentally.

In the system ether-anthraquinone examined by Smits it has always been assumed up to now that the critical line has no cusps, and that, therefore, no unmixing takes place in the unstable region[3]); it has, however, been assumed in the system diphenylamine-carbonic acid examined by Büchner that the critical line possesses two cusps in the unstable region. In the stable region the two systems exhibit, however, a perfectly analogous behaviour. The reason to assume that

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[1]) Bakhuis Roozeboom, Heterogene Gleichgewichte. II 2. (1918) S. 184. et seq.
[2]) These Proceedings. **21**. 644. (1919).
[3]) Bakhuis Roozeboom. Heterogene Gleichgewichte II. 1. (1904). S. 378 et seq.

there is no unmixing in one system, whereas metastable unmixing is assumed to take place in the other case, lies in the shape of the critical line in the stable region, in one case it is possible to join the two stable parts of the critical line by a curve with a regular, continuous course; in the other case the critical line would have to present a peculiarly steep course with a strongly pronounced maximum. This latter is deemed less probable, and can also be explained in a plausible way by the assumption that the critical line has two cusps. I will, however, point out that also metastable unmixing in the unstable region is possible for the system ether-anthraquinone, and that for the system diphenylamine-carbonic acid the metastable unmixing has not been proved, but has only been rendered probable. Hence a sharp classification of these types of binary systems is impossible.

A similar case is offered by the system sulphuretted hydrogen-ammoniac [1]). In this investigation I have theoretically examined what phenomena occur in the stable region when a critical line intersects the three phase line VLG; it was not necessary to consider metastable unmixing in that case, because it is clear that all the phenomena in the stable region can be derived from a system without unmixing. When now the experimental results of this research are examined, it appears that the critical line, when it does not possess cusps in the unstable rigion, must have a very steep course, just as that in the system diphenylamine-carbonic acid. (I have expressed this graphically in my Thesis for the Doctorate). On the same grounds that lead us for the system diphenylamine carbonic acid to the conclusion of the existence of two cusps in the critical line, the system sulphuretted hydrogen-ammoniac may be counted among the systems with unmixing. As in my opinion this system would then be the most elaborately examined example of such systems, in which besides unmixing also a compound occurs, I have indicated the second case discussed by BÜCHNER as the type sulphuretted hydrogen-ammoniac in the cited paper.

1 December 1918.   *Delft. Technical University.*

[1]) Dissertatie Amsterdam 1909. Zeitschr f. physik. Chem. **71**. 214 and 671 (1910).

Physics. — *"On the Theory of the Brownian Movement. Appendix."* By Prof. J. D. VAN DER WAALS Jr. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of Jan. 25, 1919).

In these Proceedings L. S. ORNSTEIN and H. C. BURGER [1]) advance some objections to a theory of the Brownian movement developed by me. [2]) I will briefly discuss some of them here.

I. The first rests entirely on a misunderstanding. It refers to a calculation of $x - x_0 = \Delta =$ the *measured* deviation of a suspended particle obtained in a certain *measured* time t. When determining the mean value of this quantity I omit a term with the product [3]) $\overline{x_0 w(t)}$, because this mean will be zero. O. and B. think now that I mean that the equation:

$$\dot{x}_0 \, w(t) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

will be valid for every value of t. They justly object to this, and demonstrate that this would lead to absurd results. My meaning was, however, that this equation would only hold for times that are sufficiently great. It expresses precisely the same thing as O. and B. indicate in the graphical representation on p. 924 loc. cit., namely that $w(t) \overline{u(0)}$ [4]) for t large again approaches zero. That the times in which

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[1]) L. S. ORNSTEIN and H. C. BURGER. These Proceedings, Vol. XXI, 922.

[2]) J. D. VAN DER WAALS JR. These Proceedings, Vol. XX, p. 1254.

[3]) In this w represents the force that acts on the particle. Equation (1) somewhat resembles the equation:

$$\overline{u(t) \frac{du(t)}{dt}} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

which has been repeatedly used by Miss SNETHLAGE and me in our considerations on the Brownian movement, and is among others derived by differentiating the equation $\{u(t)\}^2 =$ constant with respect to t. Equations 1 and 2, however, rest on very different considerations, and are used in a very different way, so that we should be very careful not to confuse them.

[4]) A line over a quantity denotes a mean. When no index is given, the mean has been taken over all the suspended particles. An index as here the $u(0)$ behind the line expresses that the mean has been taken over all the particles which had the definite velocity $u(0)$ at the moment $t = 0$.

the observed deviations are reached, are large enough to allow us to assume the equation for *those* values of t, is known. From this point of view my derivation is, therefore, not open to objection. [1])

II. A second objection of O. and B. refers to my assertion loc. cit. that most probably equation

$$Q \equiv \overline{w(t_1)\int_0^{t_1} w(\vartheta)(t_1 - \vartheta)\, d\vartheta} < 0 \quad \ldots \ldots \quad (2)$$

will be valid. I derive this from the consideration that $w(t)$ will satisfy the condition:

$$\overline{\int_0^{t_1} w(\vartheta)\, d\vartheta}^{\;w(t_1)} = 0 \quad \ldots \ldots \ldots \quad (3)$$

Now O. and B. are going to prove that this is erroneous. For this purpose they expand $w(t)$ into a series of FOURIER. Now it would be thought that the next step they had to take was to examine what influence the condition (3) would have on the mean value of the coefficients of this series. They do not speak, however, about equation (3), and do not subject the coefficients to any condition, and they *then* come to the conclusion that Q might just as well be positive as negative. Now it is not subject to any doubt that if $w(t)$ is not subjected to any condition, the sign of Q might be just as well $+$ as $-$. It does not require an expansion into series according to FOURIER io prove this. But the influence which condition (3) has on this sign, is left entirely unexplained by O. and B.

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[1]) How greatly Messrs. O. and B. misunderstand my meaning appears in a remarkable way from this that on one side when they think they give my views, they repeatedly enunciate theories which are in contradiction with my meaning, but that on the other hand when they think they are in contradition with my theory drawing the graphical representation in question on page 429 of their paper, they in fact but represent in drawing a course of $\overline{w(t)}^{\,u(o)}$ entirely in agreement with what I have communicated about this quantity partly in collaboration with Miss SNETHLAGE.

O. and B. admit that we were right in our contention that this curve begins with the value 0. That also for large value of t I assign the value 0 to $\overline{w(t)}^{\,u(o)}$ appears from the equation (1) discussed just now. That further for $u(o) > 0$ the value of $\overline{w(t)}^{\,u(o)}$ becomes negative for small value of t has already been expressed in the paper by Miss SNETHLAGE and me on the Brownian movement in the words: At the moment itself that the velocity w exists the force is independent of w, so on an average zero; $K_0 = 0$. After some time however a force will act which exhausts

When we inquire into this influence it must be admitted that condition (3) alone does not lead to the negative sign in a mathematical strict way. I only claimed loc. cit. to make it "highly plausible" that the sign should be negative.

If the curve which represents $w(t)$ as function of t, changes its sign only once, and therefore presents a shape of the type of fig. A,
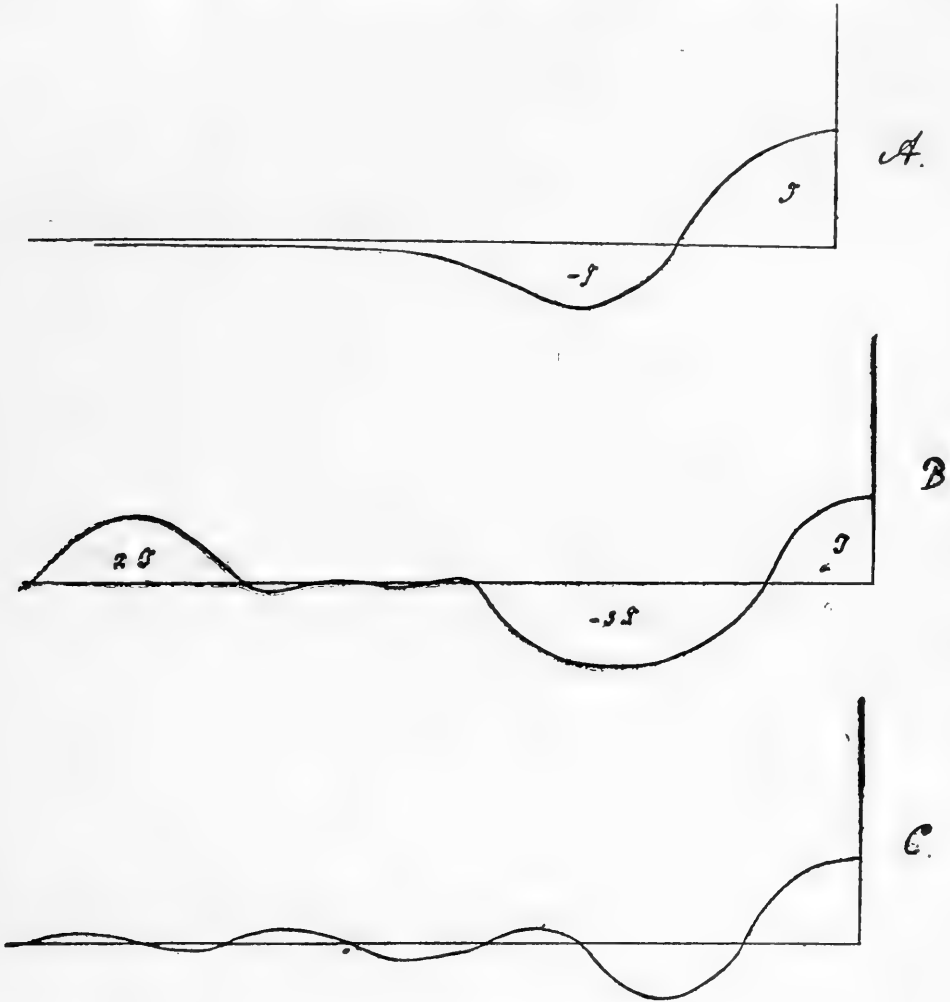
the velocity. Finally loc cit. p. 1265 the equation occurs:

$$\int_0^t w(\vartheta)\, d\vartheta = -\, \dot{x}_0$$

which as I indicate there, will be valid for not *too* small values of t, and which can hardly be reconciled with the supposition $\dot{x}_0\, w(t) = 0$ for every value of t.

$\underline{\hspace{1cm}w(t_1)}$

the sign is certainly negative. But if, as is not excluded, $w(t)$ changes its sign more than once, (3) is not sufficient to lead rigorously to the negative sign. Possibly this may be shown by the aid of an analysis according to FOURIER, but it is simpler to derive this from fig. B, where a course of the curve has been drawn which does satisfy (3), and yet yields a positive value of Q. Nobody will, however, assume a course like that. If the curve presents more than one change of sign, it will probably be represented by a strongly damped oscillating line of the type of fig. C, in which the fact that it ends with a positive part at $w(t)$ and satisfies condition (3), renders the negative sign very probable for Q.

III. One of the principal objections of O. and B. refers to the fact that Miss SNETHLAGE and I repeatedly make use of the three equations which must be considered in connection with each other, viz.:

$$\frac{1}{m}\frac{d\mathfrak{R}_x}{dt} = \frac{d^2u(t)}{dt^2} = -p\,u(t) + q(t) \quad . \quad . \quad . \quad . \quad (4)$$

$$p = \frac{1}{m}\frac{\overline{\mathfrak{R}^2\,(t)}}{\overline{u^2\,(t)}} = \text{constant} . \quad . \quad . \quad . \quad . \quad (5)$$

$$\overline{u\,(t)\,q\,(t)} = 0 . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

O. and B. assert that it follows from this that u^2 cannot be constant. When we now examine these equations, we see that (4) means only that we take $\dfrac{d^2u}{dt^2}$ for a definite particle, and add pu to it ($p = $ a positive constant that has been left undetermined for the present). As u is a function of t, this sum will also be so, and we can represent it by $q(t)$. Taken in this way this equation does not hold only for a definite moment $t = 0$, as ORNSTEIN asserts, but of course for any moment. It is an ordinary differential equation and it can be integrated without difficulty, though neither from the equation itself nor from the integral anything can be derived when it is not considered in connection with (5) and (6), which are derived as follows. We differentiate $u^2(t) = $ constant twice with respect to t and get then:

$$u\,(t) . \frac{\overline{d^2\,u\,(t)}}{dt^2} - \overline{\left(\frac{d\,u\,(t)}{dt}\right)^2} = 0. \quad . \quad . \quad . \quad . \quad (7)$$

As we can differentiate at any moment, also this equation holds, of course, for every value of t [1]).

If we now multiply (4) by $u(t)$ (*not* by $u(0)$!), if we then average,

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[1]) ORNSTEIN has repeatedly asserted that these equations do not hold for every value of t, that (4) is *no* differential equation, and that it may *not* be integrated. He has, however, never adduced any proof for these assertions. ORNSTEIN and

and if we combine the result with (7) it follows that (6) holds for every value of t, when the value of (5) is assigned to the constant p, which had been left undetermined at first.

Whereas (4) does not teach us anything, and must only be taken as a definition of q, (5) and (6) are a direct consequence of $\overline{u^2} = $ $=$ constant. And if O. and B. should succeed in proving (as they pretend they do) that it follows from the complex (4) (5) and (6) that $\overline{u^2}$ cannot be constant, they would have done no less than proving that the mathematics used are in conflict with the principium contradictionis. When their proof is examined, we arrive at another conclusion. In the first place they substitute again another equation for ours, and write $q = 0$ (for given u_0 and $\dot{u}_0$)[1]), which must no doubt mean that $\overline{u_0 q(t)} = 0$ and $\overline{\dot{u}_0 q(t)} = 0$, instead of $\overline{u(t)q(t)} = 0$, as we derived. When averaging the square of u they accordingly erroneously omit the terms:

$$2u_0 \cos\left(\sqrt{p}\,.t\right) \times \frac{1}{p}\int_0^t q\left(\vartheta\right) \sin\left\{\sqrt{p}\left(t-\vartheta\right)\right\} d\vartheta \qquad \text{and}$$

$$2\frac{\dot{u}_0}{\sqrt{p}} \sin\left(\sqrt{p}\,.t\right) \times \frac{1}{p}\int_0^t q\left(\vartheta\right) \sin\left\{\sqrt{p}\left(t-\vartheta\right)\right\} d\vartheta$$

They further expand $q(t)$ into a series of FOURIER and subject the coefficients of this series to the same suppositions as PLANCK introduced for radiation, though it is very much the question whether these suppositions hold here. For though it is true that the two curves in a certain sense are dependent on quantities determined by chance, yet there are correlations between the q's at different moments, which have influence on the mean values of the FOURIER-coefficients, which influence O. and B. have not examined.

I will not enter into other objections of Messrs. O. and B. I think that they were already beforehand sufficiently refuted by what I wrote loc. cit. In particular this refers to the objection O. and B. advance loc. cit. p. 923 to the (apparent) occurrence of a term with t^2 in $\overline{\Delta^2}$, for which compare Remark II of my article loc. cit. p. 1265.

ZERNIKE *have*, however, rightly proved that the complex of the equations (4), (5), and (6) is *not* valid, when the means are extended over a group of particles which at the moment $t = 0$ have a definite velocity $u(o)$ — and this is easy to see for $\overline{u^2}$ is not constant for such a group — but this cannot be a reason why we should not be allowed to use the complex with means over *all* particles, in which case they *are* valid.

[1]) In consequence of a difference in notation they write $\overline{w} = 0$, p. 928 loc. cit.

Physics. — *"Contribution to the knowledge of the removal of rest-gases, especially for the electric vacuum glow-lamp."* By Dr. L. Hamburger. (Communicated by Prof. Böeseken).

§ 1.   *Remarks on the action of phosphorus in the glow-lamp.*

The account of the investigations made in the end of 1916 that are discussed in this paper was already finished June 11 1917. The author postponed however the publication until the experiments together with Mrs Holst, Lely and Oosterhuis (communicated in these proceedings) had been finished.

1894 already the Italian Malignani indicated a "chemical" method technically extremely useful, to improve the vacuum of glow-lamps: viz. phosphorus.[1]) During the burning of the glow-lamp, gases may be liberated by several circumstances, especially in the beginning. When a little phosphorus vapour is present, these liberated gases will form with it under the influence of the occurring electric discharges non-volatile compounds which are precipitated on the bulb wall. (Comp. L. Houllevigue)[2]). As for this purpose quantities of 0,05 mg. are already more than sufficient this precipitate is not visible, while still the vacuum of the lamp has been much improved.

The action of the phosphorus in the glow-lamp is not very simple. The intricateness of the character of the phenomenon is still increased by the way in which the element is introduced into the lamp. Usually the filament-support of the glow-lamp is immersed in a very fine suspension of phosphorus in alcohol. When it is sealed into the glass bulb the filament and part of the supports are therefore already covered with the red phosphorus. During the sealing- in process hot air circulates through the bulb, so that it becomes very hot. This is accompanied by a partial oxydation. We must therefore also consider an eventual action of P_2O_5. But even, when this action is left out of consideration, as will be done in this paper, still the phosphorus is the cause of several peculiar reactions, which are especially connected with the above mentioned electric discharges,

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[1]) Malignani D. R. P. 82076 (1894). Substances as *As. S. J.* have also been advised, without being hardly ever used however.

[2]) L. Houllevigue, Journ. de phys. (5) **5**, 525 (1912).

which occur at the first burning of the lamp. The results of the following investigations state again, that by electric discharges the molecules are split up into components of great activity.

The energy and the velocity, observed in the processes which occur then, are astonishing. For the chemist a wide field of investigation is open here.

Already phosphorus vapour itself, without any other gas is very sensible to electric discharges. When red phosphorus is vaporized and condensed again, it is obtained in the "yellow" form. When this experiment is made in vacuo, the condensation is greatly retarded, and very easily phosphorus gets into the vacuum pump. When however on the way to the pump two small platinum wires opposite to each other are fixed, between which an electric discharge takes place by means of an inductorium, the phosphorus in precipitated there quantitatively. (Comp. von KOHLSCHÜTTER and A. TRUMKIN). [1])

This experiment can be made with small quantities of phosphorus vapour, so that the change of colour (green-yellow-red and finally very dark) with the increasing thickness of the originally extremely thin layers of the condensate can be observed. Also the forming of conglomerates in the condensate may be expected now. And further the occurrence of another modification plays of course a great part in these changes of colour.

In the following we will investigate the action between phosphorus and different gases under the influence of electric discharges. *Carbon monoxide.* Without electric discharges there is seen of course nothing, neither when the reaction vessel is heated. Quite different becomes the case, when electric discharges are sent through the reaction vessel, while at the same time the whole apparatus is heated to such a temperature that the phosphorus is vaporized. Then an extremely rapid disappearance of the gas takes place which is shown by the rapid decrease of the gas pressure (McLEOD manometer). This may be regarded as a confirmation of what has been found by the author on another occasion [2]) about a reaction between nitrogen and carbon monoxide by electric discharges viz. that the CO is split up by the discharge. Both on the path of the discharge and beside it the oxygen has occasion to oxidize the phosphorus or the liberated carbon. Where in the experiment an excess of phosphorous is introduced in vaporous state it is easy to say which of the two will be chosen by the oxygen.

[1]). V. KOHLSCHÜTTER and TRUMKIN, Zeitschr. f. Electrochem. **20**, 110 (1914).
[2]) L. HAMBURGER, Chem. Weekbl. **15**, 938—940 (1918).

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The objection might be made that the splitting up of the CO under the influence of electric discharge is accompanied already by a decrease of volume and that e.g. when Pt-electrodes are used, the metal film formed by disintegration occludes also gases. This is true and we have controlled it experimentally. Still there is an enormous difference in the velocity with which the gases are fixed when phosphorus is present or not.

We have also investigated more closely the behaviour of phosphorus with respect to *nitrogen* and *hydrogen* and found quite analogous phenomena. We must only draw the attention to the fact that the platinum disintegrated by the discharge can occlude relatively large quantities of hydrogen, so that in this case already without phosphorus a rapid decrease of the gas pressure will be observed.

In fig. 1 we have represented our measurements graphically. The ordinary lines represent the decrease of the gas pressure when phosphorus is present, the dotted ones show the behaviour when this agent is absent.
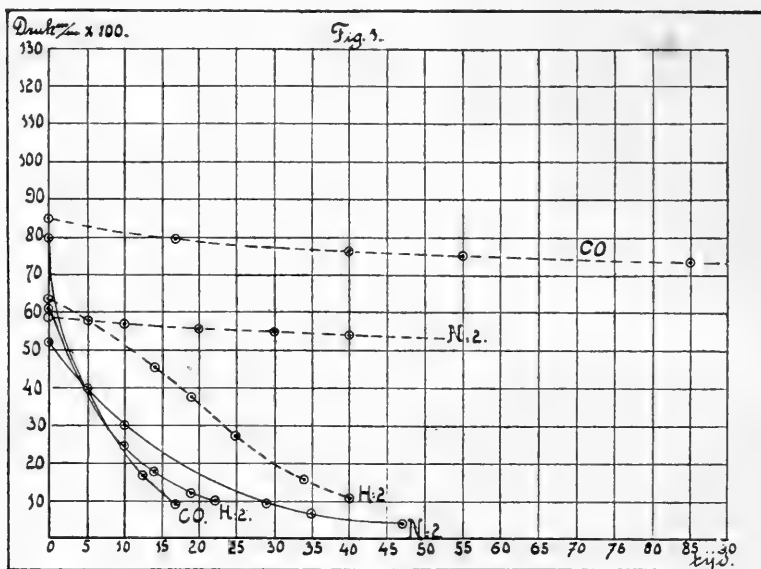
Fig. 1.

Fig. 1 clearly shows, that phosphorus can practically fix all gases very rapidly, when glow-discharges are used. In this respect its action surpasses even that of potassium, the phosphorus being able to fix even metal vapours. Moreover it is of course easier to work with red phosphorus than with potassium. In fig. 2 three spectrograms are given: the first one shows the spectrum of air, the second one that of a mixture of argon and nitrogen, with 12 % nitrogen. In the discharge

by means of an induction coil the nitrogen band spectrum dominates here also. The third spectrogram however represents the light emission of such an argon
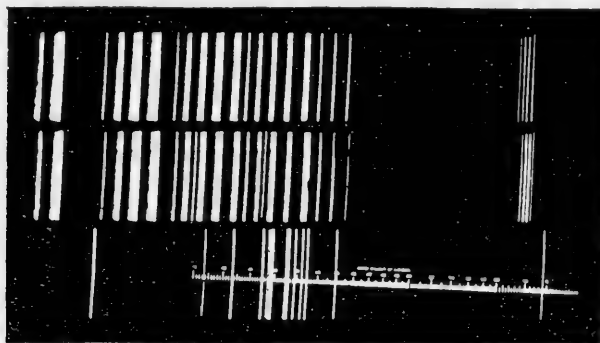
Fig. 2.

nitrogen gasmixture, when it has been exposed to the action of phosphorus (by means of glow discharges) We see, that then the argon line spectrum is observed (in this spectrogram the wavelength scale has not quite the right place). From this we may draw the conclusion, that such glow-discharges in P vapour enable us at the same time to analyze in a simple way mixtures of $Ar—N_2$.

Also in the case of the nitrogen fixation by phosphorus we must imagine the gas molecules to be first split up into atoms by the discharges, which atoms can combine afterwards with the phosphorus.

This is quite in correspondence with what R. J. STRUTT has found viz. that "luminous" atomic nitrogen can directly be bound by phoshorus. [1]

This can make clear to us why phosphorus in a glow-lamp is such a strong means to remove rest gases. Also the binding of water vapour by the phosphorus is very well observable in the glow-lamp. Unless very many precautions are taken during the evacuation of the heated lamp, it blackens much more rapidly without phosphorus than with this agent. It will be well-known that a trace of water vapour highly accelerates the desintegration of the tungsten filament, by which process the glass wall is coloured dark. That really the removal of the water vapour is the cause of the improvement is confirmed by the result found when lamps without phosphorus and with water vapour are used immersed in liquid air: no abnormal blackening is then observed.

§ 2. *On the applications of silicates.*

A. Action of the silicates.

The author has found, that when the filament is covered with

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[1] R. J. STRUTT. Proc. of the Roy London Soc. **A. 85,** 219, (1911).

silicates e.g. with glass in pulverous state instead of with phosphorus, the same action may be attained with greater security. The silicates may be applied in the same way as the phosphorus.

Several kinds of glass can be used e.g. Bohemian glass, Jena, Thuringian-, lead-glass etc. In table I the analyses of some of the kinds of glass that were used are given.

TABLE 1.

SiO_2	68.9	67.7	64.5	60.3	71.8	78.4	62.3
Na_2O	10.7	3.8	8.65	0.15	11.2	1.6	7.2
K_2O	8.2	2.5	0.60	9.5	8.2	9.8	5.0
CaO	6.2	7.7	—	—	9.8	8.2	0.1
BaO	—	10.2	—	—	—	—	—
B_2O_3	—	5.6	1.4	25.3	—	—	—
Fe_2O_3	trace	—	2.5	2.4	0.1	1.5	0.3
Al_2O_3	—	—		2.7			
ZnO	—	—	2.9	1.0	—	—	—
Sb_2O_3	—	—	2.65	—	—	—	—
PbO	—	—	—	—	—	—	23.0

B. Closer investigations.

What is the explanation of the action of these silicates? In order to learn something about this the reaction between W and glass in the glow-lamp was investigated. The first experiment that suggested itself was the following: Take a tungsten lamp with a thick wire and cover it not with glass powder, but with a glass capillary. In this way we have to do with much greater quantities of reacting substances than in the case of the lamp "sprayed" with glass powder.

As a precaution we burn the lamp for the first time under a low voltage, while the evacuated lamp was still connected with the pump. This should be done very carefully. The wire had to be exactly horizontal, in order that an eventual dripping down of the molten glass might be avoided. When by means of the electric current the wire was kept at a temperature of about 600°, all gases absorbed in the glass capillary could be removed in this way.

This process was continued until a high vacuum was kept constant during a long time. Only then the lamp was separated from the pump.

When high tension is applied to this lamp, while the wires are horizontal (see above), the glass begins so to say to boil and

vapour bubbles are developed in it. When the voltage is kept constant, this ceases after some time. When the voltage is raised further, the phenomenon of the boiling is repeated; more of the gray glass layer is vaporized. By this vaporized material the bulb wall becomes hot, especially the parts opposite to the wire. Now this material is seen to vanish gradually from the hottest spots and to be condensed in the colder ones, where it is observed as a condensate of *metallic* drops. By local heating to some hundreds of degrees these may be sublimated again.

By later experiments we have found that the metal drops are able to attack momentaneously the water in which the formed compound is solved.

When the tension is raised still further the whole lamp becomes so hot, that the above mentioned metal drops are all vaporized, at least they vanish. On cooling down the tube they are however not found back. They are solved colloidally in the precipitate on the bulb; this has obtained a light-brown colour.

The conditions under which we made these experiments were such that the quantity of glass was so great compared with that of the tungsten that not all the glass could be removed. This was however principally due to the following cause. When the temperature of the wire is sufficiently high the glass on the horizontal wire forms small spheres, which remain a long time at rest. When however the temperature of the wire is raised still further, these molten spheres become very mobile. They dance on the wire as if the spheroidal effect played a part and finally move towards the colder spots. These are found where the wire is carried by the supports. Through these much heat is namely conducted away, so that the temperature of the wire is lower at those spots. From this moment hardly any glass is vaporized.

When now on one hand the precipitate on the wall is examined and on the other hand the residue (in the neighbourhood of the supports) on the wire, the different experiments give the results collected in the following table.

<center>(See table following page).</center>

From this we may doubtlessly conclude that two processes have taken place.

a. Fractional distillation of the glass.

b. Decomposition of the alkaline-oxide in the glass by the tungsten of the wire $(W + 3 \frac{K_2O}{Na_2O} = WO_2 + 6 \frac{K}{Na})$.

C. *Fractional distillation of the glass.*

Let us consider this process *a* more closely. Then it will no longer astonish us. It confirms the view, that the glass is an undercooled fluid, in which a great number of substances (more or less volatile)

TABEL 2.

		Exp. n⁰. 1.	Exp. n⁰. 2.	Exp. n⁰. 3.	Exp. n⁰. 4.	Exp. n⁰. 5.
Precipitate on the glass wall.	mgr. KOH	15.7	13.7	26.2	Not deter- mined	19.4
	mgr. W	Only qual. determina- tion with pos. result.	0.3	10.3	10.0	4.0

Spherules on the filament. | Only qual. determined. Hardly any K_2O and Na_2O. A great deal of SiO_2; some CaO.

Remarks referring to the table. When the lamp is opened (viz. when air is left in) the principitate on the wall is found to contain K_2O and Na_2O and WO_3. For the sake of simplicity we have made all our calculations referring to KOH and W. The percentage of "KOH" was determined acidimetrically, that of W colorimetrically (Defacqz) and gravimetrically (mercuro-tungstenate).

The quantity of tungsten found on the wall in these experiments was very different. It depended to a high degree on (increases with) the temperature, to which the wire is raised finally. Especially experiment 2 shows however, that besides the alcaline percentage on the wall, caused by the decompo- sition of the glass by the tungsten, a great part of the alcaline oxide is due to a fractional distillation of the glass on the wall.

is solved. This experiment, made under very rigid conditions (in vacuo) is even a very useful confirmation of this view.

A single observation on a similar phenomenon at high temperature has been published by P. Lenard [1]. He finds, namely that when potassium-borate is glowed in a lamp, nearly all the potassium is vaporized from the pearl, while the boric acid is left behind.

Further may be mentioned that our experiments with glass had been finished, before we became acquainted with the paper of E. Anderson and B. J Nestell [2]), in which experiments are described on the vaporization of alcaline-oxides from cement- materials by heating in a Fletcher-stove to $\pm$ 1300°.

These experiments are of course very rough and influences of the gases of combustion can play a part, which is also evident to a certain degree from their observations. But for the rest their results can be regarded as a confirmation of what we found. It is remarkable, that they have also made experiments with feldspar, with a substance therefore which compared with the cement materials

[1] P. Lenard, Ann. d. Phys. (4) **17**, 204 (1905).

[2] E. Anderson and R. J. Nestell, Journ. Ind. a. Engin. Chem. **9**, 253 (1917). See also W. H. Ross and A. R. Merx Ibid. **9**, 1035 (1917).

from their other experiments contains a short age of CaO compared with the SiO$_2$ content. Moreover the vaporization was very weak. In their experiments the vaporization of K$_2$O became only detectable after addition of 50 % CaO. We, on the contrary, worked at much higher temperatures, so that, though using silicates that contained little CaO, we found still vaporization of the alcaline. But this becomes more difficult according as more alcaline has been liberated from the glass; this is of great importance for the discussion of the process mentioned sub D.

D. Reaction between the tungsten and the glass.

We have seen, that from the glass a metal is liberated soluble in water and which can easily be sublimated. This can only be potassium or (and) sodium. When the air has been let in, hardly anything but K_2O, Na_2O and WO_3 can be found on the wall by means of the flame-spectra and microchemically.

We have tried to separate the alcali-metal from the alcali-oxide formed by the fractional vaporization of the glass by sublimating in vacuo the metal by heating to a separate colder spot (a glass appendix made for that purpose). This proved however to be impossible. The alcali-metal is vaporized, but for the greater part not condensed again. It is solved in the rest of the precipitate.

Thus we were compelled to apply the following indirect method of determination.

Into a bulb A a filament (fig. 3) had been sealed. Over the W-wire a glass capillary had been slipped. The lamp carried two side-tubes, one of which a contained a small bulb g (with capillary terminals) free from gas and filled with water, while the other one b conducted via a U-shaped tube h, immersed in liquid air, and a stopcock d to the TÖPLER-pump i, to which also a GAËDE-pump could be connected for the evacuation.

First the lamp A is burnt in vacuo, while h is immersed in liquid air, so that A is free from any vapours. Then, d being shut, the lamp is loosened at the ground joint e and the small bulb g in a is shaken to pieces. Now the developed hydrogen acts on the alkali-metal, by which action hydrogen is liberated. Afterwards the apparatus is built up again, h immersed in liquid air, and by means of the TÖPLER-pump the developed hydrogen is pumped to the calibrated volume f. By means of the micro-analysis-apparatus described in another paper [1]) the volume is measured and the purity of the obtained hydrogen is controlled.

Experiment 1. Developed 412 mm^3 gas.
                    Analysis   98 % hydrogen.
This quantity of hydrogen corresponds to about 1 mg tungsten.

In fact a quantity of the order of 1 mg tungsten was found on the wall by the colorimetric method.

It is of course necessary that the water in the bulb a has been freed first in a high vacuum from solved gases. This is done most easily by connecting beforehand the small bulb with a high-vacuum-pump, freezing the boiled water

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[1]) L. HAMBURGER and W. KOOPMAN, Chem. Weekbl. **14**, 742 (1917).

and making a high vacuum, after which the ice is melted in vacuo and finally the bulb separated from the pump.

Fig.3.
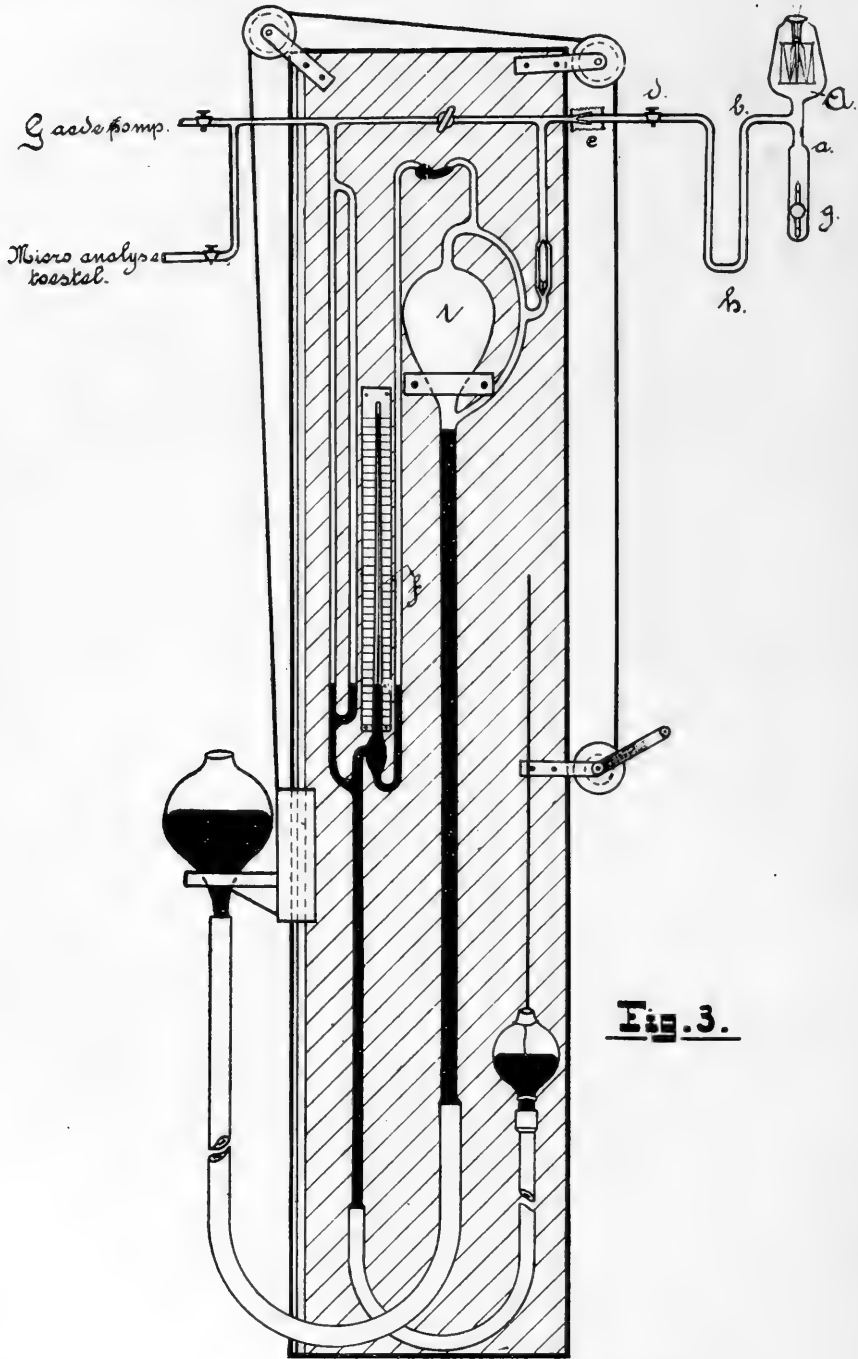
The percentage of the WO_3 found on the wall was somewhat smaller than that of the potassium. The lamp had burned however only "softly", so that probably

some WO_3 will have been left behind in the glass on the wire, probably also a trace of Ca. The alkali-metal expressed as "KOH" corresponds to 2,0 mg KOH. In fact after opening of the lamp 3,5 mg KOH was found on the wall. This surplus is due to the fractional distillation of the glass.

Experiment 2. In this experiment the vaporization of the glass was executed more strongly, so that the wall became very hot, while a great part of the formed alcali-metal was solved again colloïdally in the condensate on the wall (which was then coloured brown). At the opening of the water-bulb momentaneous decoloration was found, while relatively much hydrogen was proved to have been developed Results of the analysis: 38,2 mg "KOH", 5,3 mg "W". To this corresponds 1,9 cm³ H_2.

E. Reaction between tungsten and glass at 1000°.

From the following experiment we see that no very high temperature is necessary to show a reaction between tungsten and glass. When tungsten powder and glass powder (e.g. Thüringian glass) are mixed and then heated in an atmosphere of an indifferent gas to 1050° during one hour, we find, that the reaction has taken place.

In this way 0,65 mg WO_3 (determined by the mercuro-tungstenate-methode) was formed from 11 gr. tungsten and a few grams of glass.

From another point of view still this action between tungsten and glass is remarkable. Let us namely consider the case, that we wish to seal electric conducting wires air-tight into an apparatus of hard-glass. For this purpose we must take a metal with a small dilatation coefficient, such a metal is the tungsten. During the sealing- in this is covered however with a layer of oxide and when this remained in this state it would prevent, as has been found experimentally, the connection between glass and wire from becoming air-tight. At this temperature however tungsten and the lower tungsten-oxides act on the glass; the oxides do not remain therefore oxides and without any further precautions a very sufficient shutting-off is obtained (Comp. also E. WEINTRAUB). [1]

F. *Can the action of the silicates be replaced by alcali-oxides?*

The reaction between tungsten and the glass capillary in the lamp is principally based upon the transformation:

$$W + 3 \frac{K_2O}{Na_2O} = WO_3 + 6 \frac{K}{Na}.$$
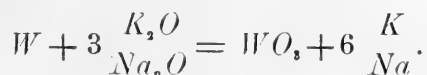
When a lamp is made, however, in which the filament is covered not with glass, but with Na_2O [2]) we have practically found nothing of such a reaction.

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[1]) E. WEINTRAUB, U. S. patent 1. 154. 081.

[2]) Comp. L. HAMBURGER, Chem. Weekbl. **13**, 516 (1916).

This can easily be explained. In the high vacuum the Na_2O is very volatile on a moderate rise of the temperature, so that it is vaporized from the incandescent wire, before it has had time to react to an observable degree. The activity of the Na_2O (K_2O) in the glass is due to the fact that Na_2O (K_2O) when solved in the glass can act on the tungsten in the evacuated space at a much higher temperature than would be possible with the free oxide because of its volatility.

This is analogous to what is known of the $KHSO_4$ which, used in analytic chemistry, is so much more active than SO_3, because at high temperatures the SO_3 in the $KHSO_4$ can still be active in the condensed state.

Doubtlessly however the tungsten acts also on the Na_2O when the temperature is so low, that this substance is hardly distilled. This has been mentioned in the literature (comp. GMELIN-KRAUT, Handbuch etc.) and moreover we have stated it by experiments. P. LENARD (l. c. p. 201) already has shown that in the oxidizing part of the BUNSEN flame a metal like platinum is rapidly attacked by oxides and hydroxides of the alkalines, further also by carbonates and sulfates of the alkalines.

G. Conclusions.

By these experiments we have obtained sufficient data to understand, why glass can replace the action of phosphorus.

Partly this is due to the fact that by the fractional distillation, substances (alcali-oxides), are formed in extremely fine particles (vapours), which are able e.g. to fix traces of humidity. But moreover free alkali metal is formed. This is very important; for when for the first time the lamp is burned more or less strong electric discharges take place, as was mentioned already above. Now, the alcali metals are very active, but especially when electric discharges are sent through the lamp. G. GEHLHOFF[1] has shown namely that the application of the action of alcali metals in glow-discharges forms one of the quickest methods for the preparation of pure rare gases.

Conclusion: In the form of glass a substance very inactive at room-temperature is introduced into the lamp, from which at high temperatures, however, the free alkali metal is developed as a vapour, and under the influence of electric discharges this can cause the

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[1] G. GEHLHOFF, Verh. d. Deutsch, Phys. Ges. 13, 271 (1911).

same action as the small quantities of phosphorus that are necessary to remove the rest-gases.

§ 3. *On the condensate, formed by the vaporization of very small quantities of silicate. Prevention of the blackening of the bulb wall.*

In our experiments with the glass capillary we have seen, that from the glass principally only the alcaline-oxides are found on the wall. In the technical glow-lamp this is however not the case. There the quantity of glass powder on the incandescent body that is required, is so small, that in a moment everything has passed to the wall, where the precipitate has again a neutral character. Another question however is, whether the glass formed in this way on the wall, is the same as that which covered the incandescent body. Though the whole process lasts very short, still the sublimation must have been fractional and the cooling down must have taken place exceedingly rapidly. In fact the glass on the wall is different. Perhaps it consists of different layers of different constitution. At all events the alcalines are bound more loosely. They are solved more easily than the alcaline from the original glass. When the lamp is subjected to *Tesla*-discharges a *sharp* flashing of the wall is oberved. Spectroscopically the sodium-lines are seen very intensive. With ordinary glass this is not the case. Under special conditions crystallization may take place, when the lamp is opened. Analogous changes form a separate dominion of investigation [1]).

Besides the removal of the rest-gases from the glow-lamp the glass that covered originally the incandescent body exerts still another action. We have seen above how by the condensation on the bulb-wall no "normal" glass is obtained. P. P. von WEIMARN [2]) already has remarked that the specific weight of the glass is smaller according as it is cooled more rapidly. The distances of the molecules in such a glass would therefore be much greater than in the normal glass. In these proceedings Messrs. L. HAMBURGER, G. HOLST, D. LELY Jr. and E. OOSTERHUIS have published a communication, in which it is investigated, how certain solid substances, when applied in a thin layer on the bulb-wall, can prevent the darkening of the wall (a consequence of the condensation of vaporized tungsten from the incandescent filament). This decolorating action is proved to have a

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[1]) W. REINDERS and L. HAMBURGER. These Proceedings **25**, 661 (1916), **26**, 595 (1917).

[2]) P. P. von WEIMARN, Zeitschr. f. Chem. u. Ind. d. Koll, **9**, 25 (1911).

physical character. When the tungsten molecules are kept apart from each other by the molecules of another substance, the strong absorption of the light by a continuous tungsten layer can be prevented.

This action is also shown by the "glass" on the wall. While the smooth bulb-wall itself is evidently inactive, the "porous glass" coming from the incandescent body proves to be able to envelop the tungsten particles that are shot into it. When however the lamp has been opened, so that the porous glass can crystallize, it has lost much of its activity.

§ 4. *Aluminates, phosphates, oxides:*

It has been remarked already several times (comp. e.g. Chem. Weekblad **13**, 536 and seq. 1916), that part of the troublesome gases in a glow-lamp are only liberated when at the first use of the lamp the wire has reached a high temperature. For this reason it is desirable to use substances which at that high temperature are vaporised only relatively slowly from the wire. In our experiments we have found such materials in silicates, several kinds of glass, feld-spar esc. But besides by silicates *this condition is also fulfilled by aluminates*, as e. g. magnesium-aluminate, further also by $Cu_3(PO_4)_2$ (when not hydrolyzed) and other similar compounds.

Our first experiments on magnesium-sulfate were made with spinel, which we obtained from a well-known firm. The above mentioned property was found again. The analysis showed however, that the composition was:

SiO_2 39,3°/₀, Al_2O_2 22,5°/₀, Fe_2O_3 6,3°/₀, CaO 34,3°/₀, MgO 0,2°/₀.

It could therefore not be called spinel. Still this experiment was very instructive. It showed namely that the presence of alcaline-oxide was not absolutely necessary to obtain the effect. Later on we will return to this.

The natural spinel that was at our disposition being thus no true spinel, we made artificially a compound by heating MgO and Al_2O_3 to 1800°. The product really showed the action discussed above. We also tried other substances in this respect. When the temperature is only sufficiently high and the layer on the incandescent body sufficiently thin it is evident that all foreign substance on the wire can be vaporized. Thus the CaO — when such a silicate is used — from the glass will be sublimated on the wall under these circumstances. And then it is of course probable, that also some free Ca-

metal will be formed, which will not be less active than the alcaline-metal.

Finally we may ask, whether not many more substances possess the "phosphorus-replacing" action. To try this lamps were constructed in which the incandescent body had been sprayed with different oxides. We tried ZrO_2, ThO_2, TiO_2, SiO_2, CaO, Na_2O.

With all a strong glow-discharge took place at the first burning. The SiO_2 only made an exception. Though the activity was less than in the case of the glass-powder, the silicium-dioxide gave satisfactory results.

This suggests, that also the SiO_2 is decomposed a little first, so that silicium is liberated, which can replace the phosphorus. Later on the SiO_2 on the wall can of course prevent again the blackening (comp. § 3).

The percentage of SiO_2 however that is decomposed in the "sprayed lamp" is very small compared with the principal mass of this substance, which is vaporized without having been decomposed, then condensed on the wall, where it prevents the blackening.

In order to learn more about this we have drawn out quartz-tubes to capillaries and slipped these over the tungsten wire. When now the tungsten wire is glowed in vacuo at a high temperature, a relatively slow vaporization of the SiO_2 takes place. Finally however a considerable precipitate is obtained, which strongly shows the interference colours. When the bulb is opened, gradual changes are observed of the quartz which forms such a thin layer. Everywhere needles are formed stretched in one direction, which also show interference-colours, but in which already with the naked eye irregularities are seen; with 50-fold magnification already a shell-shaped conglomeration-structure of those needles is observed. Sometimes such an alteration remains very local; doubtlessly it is due to the difference in dilatation-coefficient of the glass (under layer) and the quartz (upper layer)[1].

In a following series of experiments the temperature coefficient of the resistance of the wire was investigated to find out whether it had taken up some Si at the supposed decomposition of the SiO_2.

It will be known, that the temperature-coefficient of the resistance offers an extremely sensible method to see whether an element contains any impurity. Tungsten and silicium allie very easily, so that the formation of Si must become evident from the change of the temperature-coefficient of the resistance.

Only very little silicium however is needed to remove rest-gases (with the aid of glow-discharges). Let us suppose for the sake of simplicity, that the only rest-gas that occurs is oxygen with a total pressure of 0,006 mm; in a bulb with a volume of 150 cm³ this would correspond with 0,0017 mg O_2, which could only be bound by 0,0015 mg Si.

Little silicium is needed not only, but little silicium is formed also in the lamp. That is why the method of the temperature-coefficient measurement does not give a positive indication on the formation of Si; this is also due to the fact that the

[1] Also R. B. SOSMAN (Journ. Ind. and Engin, Chem. 8, 985 (1916) states at condensation of quartz-vapour a pronounced inclination to form needles of amorphous quartz.

tungsten wire must glow strongly for the formation of Si from SiO_2, so that the small quantity of Si that might eventually be formed, will directly be vaporized again. It will therefore be better to arrange the experiment with the quartz capillary, in such a way that we investigate whether more tungsten in the form of WO_3 is precipitated on the wall than in a lamp without quartz. In fact we then obtain a positive result, but the quantity of WO_3 is smaller than when glass is used. That reaction between W and SiO_2 is analogous to that between C and quartz, by which reaction according to W. Hempel [1]) reduction to Si and formation . of CO take place.

An intensive reaction between SiO_2 and W does therefore certainly not take place in the lamp sprayed with SiO_2-powder. The good influence at the first burning is therefore also much smaller with quartz than with glass, so that already for small quantities of impurities that develop gases, the activity of the SiO_2 is insufficient.

Metal-oxides as ZrO_2, ThO_2, TiO_2, Na_3O are not fit to replace the action of phosphorus. Either they give rise to a glow discharge at the first burning of the lamp (by which the lamp can be destroyed) or (as in the case of Na_2O) they are vaporized before those elements can be liberated, which possess the same activity as the phosphorus. Besides, traces of impurities, which can accompany such substances as Na_2O, lower the degree of the vacuum, of the oxides mentioned above SiO_2 only can be used. But this is a non metallic oxide that intensively emits electrons or ions before or during the decomposition.

Is there no metal-oxide, less volatile than Na_2O, which does not at all or hardly increase the glow-discharge at a high temperature? Perhaps Al_2O_3 might be useful. This oxide however with the well-known affinity between aluminium and oxygen is very stable at high temperatures and at all events did not show the activity that was wanted. A different result was obtained with MgO. In fact this shows the phosphorus-activity in a sufficient degree.

The application of glass remains however the simplest method. It is somewhat paradoxal, that we only need to rub the bulb of a glow-lamp to powder and to spray the filament with it to obtain a better lamp after sealing it into a new bulb. But this paradox may have found an explanation in the preceding discussion.

It may still be remarked that we need not confine ourselves to the use of the mentioned substances. We can also apply these in combination with others, the good activity of which is known. It is however remarkable, that the combination glass-powder + phosphorus gives less satisfactory results. At the first burning of the lamp the phosporus acts perhaps reducing in the vaporizing glass, which causes already a little blackening of the precipitate on

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[1]) W. Hempel, Zeitschr. f. angew. Chem. **30**, 10 (1917).

the wall. After the finishing of the first burning we see namely on the bulb wall already a slight but detectable black colour.

§ 5. *Summary.*

1. By investigations in the spectrographic way and by determinations of the changes in the gas pressure it was shown that with the aid of electric discharges phosphorus vapour can be brought to a rapid reaction with all gases except with the inert gases.

2. The action, obtained in the glow-lamp with phosphorus, can also be observed with silicates.

3. At high temperatures silicates undergo a fractional distillation.

4. When tungsten and silicates are in contact at a high temperature a reaction takes place between these substances, by which alcaline-metal is liberated. By means of this we can in the same way as with phosphorus obtain the perfect removal of rest-gases (in glow-lamps) with the aid of electric discharges.

5. The reaction between tungsten and glass makes the use of tungsten for leading- in wires possible.

6. At a rapid cooling of the vaporized silicate a product is formed in an undercooled state, which has other properties than the normal glass. The thus obtained condensate can decrease the blackening of the wall in the glow-lamp, due to the vaporized tungsten.

7. A similar reaction as with silicates is obtained by the application of aluminates, calcium-phosphate, magnesium-oxide, silicium-dioxide. In the case of this last oxide we come to the conclusion that a trace of free Si is formed; only quantities of the order of magnitude of 0,001 mg. Si show a detectable activity.

Physics. — *"On the influence of different substances on the absorption of light by thin tungsten layers"*. By L. Hamburger, G. Holst, D. Lely and E. Oosterhuis. (Communicated by Prof. H. Kamerlingh Onnes).

Introduction. The investigation that will be communicated here shortly, refers to a subject of great importance for the glowlamp industry viz. the prevention of the blackening during the burning of vacuum tungsten lamps.

It is well-known, that the efficiency of such a lamp increases, as the temperature of the wire is raised. Now in this way a very high efficiency may be obtained in the beginning, but by the vaporization of the filament, which increases exceedingly rapidly with the temperature, the glass bulb is covered with a thin layer of tungsten, which can absorb so much light, that after a short time the economy of the lamp sinks below that of a similar lamp that burns at a less high temperature.

Of course, many methods have been tried to prevent this blackening of the bulb. The means that have been applied may be divided into two groups.

1st. It is tried to decolorate the tungsten precipitate by the introduction of certain substances, so that it becomes less inconvenient.

2nd. The velocity of vaporization of the tungsten is decreased by the introduction of a gas under high pressure. This last method is applied in the so-called half-watt lamps.

Here however we shall exclusively treat the first method and investigate by what substances the blackening of the vacuum lamps can be prevented and in what way these substances act.

Two principal groups of substances may be discerned.

1st. Gases which are chemically active with the vaporized tungsten and form with it a less coloured compound, and substances which during the burning of the lamp develop active gases.

2nd. Substances of which we cannot simply say that they are chemically active with the vaporized tungsten.

This last group especially will be discussed here. First we must however make some remarks on the first.

§ 1. *Action of gases or substances which develop gases by dissociation.*

The simplest action is that of small quantities of gas that are introduced into the bulb. In this respect especially chlorine and oxygen are remarkable.

LANGMUIR [1]) has shown, that at room temperature and even at 200° chlorine acts hardly or not at all upon the tungsten precipitate on the bulb. When a small quantity of dry chlorine is introduced into a lamp, in which a tungsten precipitate has been formed already on the bulb, the chlorine will not act upon it. When however the lamp glows, the tungsten precipitate vanishes rapidly. LANGMUIR explains this by the assumption that the chlorine is dissociated by the glowing wire; the very active chlorine atoms which at the low pressure of the chlorine fly directly to the walls of the bulb, act upon the tungsten and form with it the colourless WCl_6.

One might think, therefore, that by the introduction of a small quantity of chlorine the lamp could be improved. The result, however, does not answer this expectation, as the pressure of the chlorine necessary to double the life [2]) of a normal lamp must be not less than ½ mm. [3]).

At this pressure the chlorine cannot act in the above mentioned way, the free path of the atoms being much too short. A reaction between the tungsten *vapour* however and the chlorine will be possible, which can prevent the formation of a tungsten precipitate. Such a gas filling however offers several difficulties.

At a pressure of ½ mm. the conduction of heat by the gas is already rather high, which lowers the efficiency, while at least at the higher voltages electric discharges through the lamp, which might destroy it, are not excluded. But moreover the tungsten vaporizes gradually only, so that already before a considerable tungsten precipitate can be formed, the chlorine will have destroyed the lamp by other reactions.

LANGMUIR found namely that also without dissociation of the halogen reactions may take place between W and Cl. The velocity of reaction is greatest at ± 1500° K., greater than at higher and

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[1]) I. LANGMUIR, Journ. Amer. Chem. Soc. (37), 1142, 1915.

[2]) By the life is generally understood the time in which the intensity of the light is decreased by 20%.

[3]) The quantity of tungsten e.g. which is vaporized in a 110 Volt and 50 can dle lamp and which absorbs 20% of the light is about 0,26 mgr. To form with this WCl_6 0,3 mg. chlorine is necessary, corresponding to a pressure of ± ½ m.m.

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lower temperatures. At the high temperature at which the filament glows, practically no reaction takes place as according to LANGMUIR the intermediate products necessary for the formation of WCl_6 are dissociated again (under formation of Cl atoms) before the reaction by which WCl_6 is formed has been completed.

There are however always parts of the filament and often also of the tungsten supports that carry the wire, at a temperature, at which the velocity of reaction is great. These parts will be acted upon amidst the formation of WCl_6. In a lamp filled with chlorine the wire, when glowing only weakly, was really found to be soon corroded, while WCl_6 was condensed on the wall opposite to the wires. When on the contrary the wire glowed at higher temperature it remained nearly intact, while WCl_6 was precipitated on the wall opposite to the supports. The diameter of the wire increased even, after 5 minutes the electric resistance was decreased by $12°/_0$. This can easily be explained. By the high conduction of heat of the gas the wall of the bulb is heated. The WCl_6 is vaporized and dissociated at the glowing wire, leaving behind on it a small quantity of tungsten, while the chlorine is again liberated. The wire thickens at the expense of those parts of the lamp that have a temperature at which the velocity of reaction is great and the lamp is soon destroyed.

Thus the chlorine describes a kind of cycle and we may ask whether it would not be possible to introduce much less chlorine into the lamp, so little, that those parts that have the temperature of the maximum velocity of reaction are not destroyed after a few hours, but only after nearly 1000 hours by the action of the chlorine.

When however the pressure of the gas is lowered, the conduction of heat decreases, the glass wall becomes less warm, the WCl_6 that has been formed is no longer vaporized and no chlorine is formed back. In fact it was proved that in this way nothing could be reached. After a short time all the chlorine in the bulb was fixed and lamps with small chlorine fillings behaved after a short time as if not any chlorine was present.

The other halogens and oxygen behave in a similar way. By the low vapour pressure of WO_3 there is here still less question of a cycle.

Better results were reached by the introduction of substances into the lamp, which during the burning develop continually small quantities of chlorine or oxygen. F. SKAUPY was the first who suggested this method. A small quantity of potassium-thallium-chloride is introduced in a tube in such a way into the lamp, that during the burning its temperature becomes high enough to develop chlorine.

The quantity of salt is thus chosen that the chlorine pressure does not become either too high or too low. Not too high for the above mentioned reasons; not too low as then the action is insufficient. We have been able to state that K_2TlCl_6 develops chlorine at 350° C. already. A small quantity of the salt was introduced between the 2 glass walls of a Dewar-glass filled with liquid air, the external wall of which was heated to 350°. The distillate formed in the high vacuum and precipitated on the cold inner wall contained rather much free chlorine and further thallium chloride; potassium chloride was not found in it.

The good results reached with this salt in the lamp may therefore doubtlessly be ascribed to the continual presence of a chlorine atmosphere of very low pressure, by which the tungsten precipitate is converted into WCl_6, which is only very weakly coloured. A similar action can be stated of copper- and silver-chloride and also of some chlorates and oxides that are easily decomposed as e. g. barium chlorate, barium peroxide, higher lead oxides.

§ 2. *Action of solid substances that are not easily dissociated.*

The action of the above mentioned substances was easily explained by their dissociation. Now H. H. Needham has found, however, that also a substance as cryolite when applied to parts of the lamp that have a temperature between 400° and 800° gives good results, while from other sides the application of small quantities of sodium chloride to the glowing body is recommended. In fact such lamps with cryolite or sodium chloride prove to blacken less quickly than ordinary vacuum lamps. Needham supposes the cryolite to be decomposed, so that in the lamp a "certain" halogen atmosphere is formed to which the obtained result would be due. As the occurrence of such a halogen atmosphere seemed improbable to us, we subjected this phenomenon to a closer investigation and have made several experiments which might give us a better insight into the action of these substances. First we investigated, whether sodium chloride could act in the same way as K_2TlCl_6. When introduced in a small tube into the lamp, the NaCl proved however to be perfectly inactive, as might be expected. When sprayed however on the wire and the supports it was very active. When only the supports were sprayed the action was again rather small. The salt on the filament must therefore be the active part. As soon as the lamp glows, however, it is vaporized and condensed on the glass wall. This can easily be seen by

opening such a lamp.[1]) When namely the moist air comes into the bulb the salt is seen to crystallize on the wall. When therefore the decolorating action is due to a development of a halogen this thin salt layer must, during the burning of the lamp continually develop small quantities of chlorine. Neither by heat, nor by the action of light sodium chloride develops chlorine. From the investigations of GOLDSTEIN[2]), and WIEDEMANN and SCHMIDT[3]) it was known however, that Na Cl is influenced by cathode rays. We have therefore considered the possibility that the electrons, emitted by the incandescent wire, might have a similar action. This was proved not to be the case.

When electrons of high velocity impinge upon a NaCl layer, a coloration of the salt is seen; brown or violet according to the velocity. The brown salt is decolorated again by the action of the day-light, the violet again is light-proof. GOLDSTEIN assumes now that this coloration is due to a physical action, while WIEDE-MANN and SCHMIDT came to the conclusion that the salt is decomposed and that then the formed sodium or sodium sub-chloride is solved colloidally in the surplus of salt. Only in the latter case there can be question of the formation of a halogen atmosphere. A closer investigation taught us that in the case of the brown salt no chlorine had been developed from the solid phase; it acted neutrally; in the case of the violet salt on the contrary a decomposition has taken place.

As it has now been proved that $NaCl$ can be decomposed by an impact of electrons we have put the question what velocity of the electrons would be necessary for this. Hypothetically we have assumed that the electrons would possess this energy, when their kinetic energy is greater than the heat of formation of the salt. For $NaCl$ this heat amounts to 97,6 kg. cal. per Gram. mol. and thus to $0,676 \times 10^{-11}$ erg for a molecule. In this case electrons with a velocity above $1,23 \times 10^8$ cm/sec. would be able to bring about a decomposition. Electrons with such high velocities really occur in the lamp. We were able to prove this by means of a lamp with a side tube which contained a FARADAY cage. At the normal burning temperature the charge was always —5.7 Volt with respect to the negative pole of the filament. This proved that electron velocities of 1.40×10^8 cm/sec. really occur.

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[1]) In these experiments the thickness of the layer was about $1—2 \times 10^{-6}$ cm., viz. about 50 molecules.

[2]) E. GOLDSTEIN, Wied. Ann. (54), 371, 1895 and (60), 491, 1897.

[3]) E. WIEDEMANN and G. C. SCHMIDT, Wied. Ann. (54), 604, 1895; (56), 201, 1895 and (64), 78, 1898.

The action could however be influenced [1]) neither by the application of an accelerating or a retarding field nor by means of a solenoid. Moreover it is not probable that the number of electrons with velocities above 1.23×10^8 cm sec. is sufficient. When no accelerating or retarding electric fields existed in the lamp, there would be at the normal glowing temperature of 2350° abs. only one such an electron to every 250 vaporized molecules. In reality the electron current is much smaller than the saturation current, so that doubtlessly the number of high velocity electrons will be still smaller. A decomposition of the salt by the impact of electrons is therefore very improbable. But moreover we could prove directly, by a chemical method, that in the lamp no decomposition of the $NaCl$ takes place.

A lamp with a side-tube was constructed. During the burning the side-tube was immersed in liquid air. After the experiment no trace of a chlorine condensate was found to be present. A drop of mercury at the bottom of the tube did not leave a trace, when shaken, as is always the case when traces of chlorine are present. Further the rest of the salt should react as a basis. But even with the method of F. MYLIUS and F. FÖRSTER with 0,001 normal solutions and iodine-eosine as an indicator we were not able to find an alteration in the alkalinity of the salt. Evidently no decomposition of the salt takes place.

Further we stated that the salt was just as active when the burning lamp was immersed in liquid air. This made it exceedingly improbable that we had to do with a decomposition of the salt and the decolorating action by a halogen atmosphere. Moreover it was proved that also other halogen compositions as $Na\,Br$, KI are just as active at the temperature of liquid air as at room temperature, while for Br and especially for I an exceedingly small activity might be expected at liquid air temperature.

We also considered the possibility that the *velocity of vaporization* of the tungsten might be *lowered* by the formation of a covering layer of salt. M. KNUDSEN [2]) had stated a similar decrease of the velocity of vaporization in the case of impure mercury and I. LANGMUIR [3]) found in his investigations that even at 3300° K. during some time tungsten can remain partially covered with a layer of oxygen (of atomic thickness). It is therefore not excluded that a

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[1]) In these investigations we could state that the vaporized W particles are not charged.

[2]) M. KNUDSEN, Ann. d. Phys. (47), 697, 1915. .

[3]) I. LANGMUIR, Journ. Amer. Chem. Soc. (38), 2221, 1916.

little salt is left on the wire which prevents the vaporization. We found however that at equal temperatures a sprayed and a non-sprayed tungsten wire show an equal increase of the electric resistance by the decrease of the wire diameter, and equal loss in weight, while in both cases, the tungsten condensate on the wall of the bulb has the same weight. We thus come to the conclusion that the $NaCl$ is active in its solid phase and that in contrast with what we have seen in the case of $K_2 TlCl_6$, the decoloration of the tungsten is not due to free chlorine.
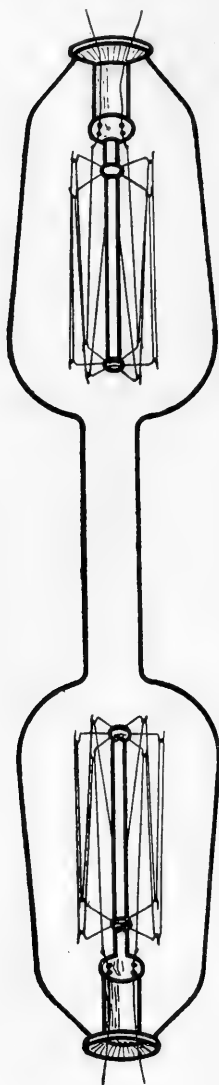
The difference between the behaviour of $NaCl$ and $K_2 TlCl_6$ is especially evident by the following experiment, in which a double-lamp was used. When the wire in the inferior lamp is covered with $NaCl$, but not that of the upper one, the inferior lamp is found to blacken much less rapidly than the upper one. When the experiment is repeated with a similar combination, in which the inferior lamp contains a small quantity of $K_2 TlCl_6$ instead of $Na Cl$, such a difference is not observed. The action of the $NaCl$ is therefore local in contrast with that of $K_2 TlCl_6$. The chlorine developed by this latter substance is spread over the whole bulb and attacks the tungsten precipitate both in the inferior and in the upper part.

What may be the action of the thin salt layer on the wall of the bulb upon the vaporized tungsten?

Is the observed decoloration due to the formation of some less coloured chemical compound or do the $NaCl$ and W remain on the wall chemically unaltered, while they only give an arrangement which absorbs less light?

Fig. 1.

The following experiments render it probable that we have not to do with a chemical action. Firstly we stated, that also with other metals a decoloration of the precipitate was found e.g. C, Mo, Pt, Fe, Ni, Au, Cu, Ag gave all both at room temperature and at liquid air temperature less dark precipitates when the wall of the bulb was covered with a thin salt-layer than when this was not the case. A chemical action at low temperature between Au and $NaCl$ e.g. may doubtlessly be considered as excluded. Moreover it was found that not only $NaCl$, but nearly every other stable

compound gave rise to a decrease of the light absorption of the vaporized tungsten. In this respect we have obtained good results with Na_3PO_4, Na_2WO_4, KCN, Na_2O, NaF, CaF_2 and with many other substances.

In the following way we still made it probable, that the vaporized tungsten was present unaltered in the $NaCl$ layer. When H_2O was introduced into the lamp a quantity of hydrogen was developed. As we had found already before that the $NaCl$ did react neutrally, so that there was no free Na, this development of hydrogen must be due to the presence of free W.

While therefore the action of the salt layer depends little on its chemical composition, the state of the salt on the wall often proved to have influence. When much more salt was introduced into the lamp, a white crystallized precipitate was formed just as on the introduction of moist air. In this form the salt was much less active. Lamps, the bulb wall of which is covered with salt crystals, are not much better than those that do not contain any salt. A similar phenomenon is observed with *glass*. When this is brought in small quantities on the wire in pulverous state, and when this is distilled on the bulb wall, this fine distillate shows a similar action as $NaCl$, while the smooth bulb wall evidently is inactive. Still we cannot generalize and say, that crystallized substances are inactive. With crystallized NaF and KCl e.g. good results were obtained though not so good as when these substances were in the amorphous state.

In general however it was proved to be of importance for the decolorating action of the salt that it was present on the wall in a very finely divided state. Now it is probable, that the W particles coming with a relatively high velocity from the wire, will penetrate over some distance into the salt and stick then in this layer in an extremely disperse state. That in a similar state the light absorption can be very small, had already been found by v. WEIMARN [1]) for colourless gold-glass and gold-quartz and by ZSIGMONDY [2]) for colourless colloidal gold-solutions, while v. WEIMARN [3]) and Mc. INTOSH and EDSON [4]) have pointed to the phenomenon that colourless colloidal solutions can be obtained by rapid cooling of true solutions. The particles are then prevented from forming greater conglomerates. By means of the

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[1]) P. v. WEIMARN, Zeitschr. für Chem. und Ind. der Kolloïde, (11), 287, 1912.

[2]) R. ZSIGMONDY, Zur Erkenntniss der Kolloïde, 1905 and Zeitschr. für phys. Chemie, (56), 65, 1906.

[3]) P. v. WEIMARN, Grundzüge der Dispersoidchemie, p. 70, 1911.

[4]) D. Mc. INTOSCH and R. EDSON, Journal Am. Chem. Soc. (38), 613, 1916.

ultra-microscope REINDERS and HAMBURGER [1]) have investigated the extremely thin metal and salt layers formed by vaporization. For CaF_2, which was used in many of the following experiments, they found the field optically empty. Also for tungsten layers the field was optically empty, as well in the case that tungsten was condensed directly on the wall, as when the tungsten particles stick in a salt layer. With the ultra microscope there could thus be found no difference between a lamp treated with salt and an ordinary one. For metals with a lower melting-point as silver, the molecules of which have a greater mobility, a difference was found. A thin silver layer precipitated on glass showed ultramicroscopically a close network of ultramicrons. When the silver is precipitated upon a salt layer (CaF_2) the field was found optically empty. The presence of the salt prevents therefore the molecules from forming conglomerates. They evidently lie dispersed through the salt, so that the action of the latter is due to its keeping the metal molecules separated. We have examined more closely the question, how this influences the absorption of the light and investigated, whether the optical behaviour of such a thin layer might be closely connected with its electrical conductivity. For this purpose we have made a series of measurements on the conductivity of these layers and really found, that in a lamp with salt much more tungsten must be vaporized before an electrically continuous layer is formed than in lamps
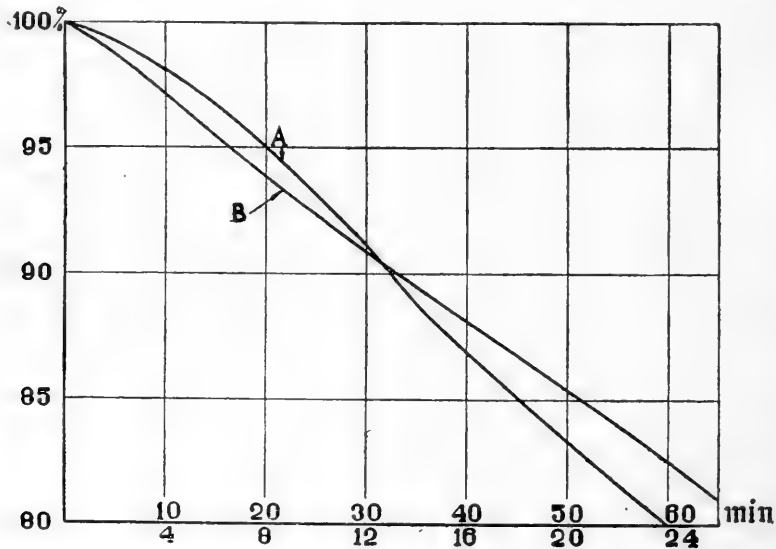
Fig. 2.

[1]) W. REINDERS and L. HAMBURGER, These Proceedings.

without salt. We thought now that the action of the salt might be explained in this way, that the electrically still separated molecules behave optically more or less as separated molecules and give like gas molecules a line absorption spectrum, while only when their mutual distances have become so small that the electrical conduction sets in, also metallic absorption is observed. This proved however not to be the case. Long before an electrically conducting layer is formed, a grey colour and metallic absorption are found.

In fig. 2 the intensities of a lamp without salt (A) and of one with salt (B) have been represented as functions of the time. The temperature of the wire was about the same in both lamps [1]). The diameter of the wire had been thus chosen that its decrease by vaporization had no appreciable influence on the candle power. The lamp that was used is represented in fig. 3. In order to age the lamp it was first burned during some time with the inner glass cylinder high up, so that no tungsten could reach the cylinder wall. Then the cylinder was lowered again and the intensity measured with definite intervals with a thermo-pile through a $CuCl_2$ filter. In this way much more accurate results could be obtained than by photometric measurements.
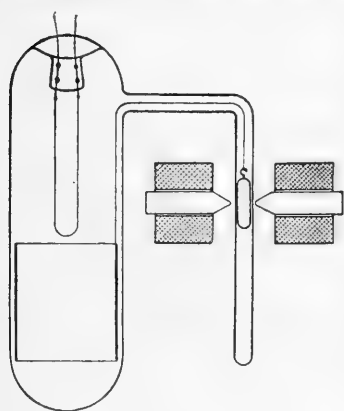
Fig. 3. Now it has been proved, that also in the lamps treated with salt the formed tungsten precipitate absorbs from the very beginning and that the absorption is nearly proportional to the number of the vaporized W-molecules. In the lamp without salt the curve shows in the beginning a typical change of inclination, which could be rather well reproduced.

In these thin layers we have evidently to do with a phenomenon analogous to that mentioned by STARK [2]), when he speaks of the carriers of the spectral lines and assumes electrons that are optically free but electrically bound.

The phenomenon has however to be investigated much more thoroughly before an insight will be obtained of what takes place in these thin layers. We still want to mention the following experiment. In a lamp immersed in liquid air a thin layer of chlorine was

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[1]) In the figure the numbers above the abscissae refer to (B), those below it to (A).

[2]) STARK, Jahrbuch der Rad. und El. (14), 139, 1917.

condensed on the bulb wall, upon this the tungsten was precipitated. At the vaporization of the chlorine, when the lamp had been taken out of the liquid air, the layer was torn in two over a length of some centimeters, while the metal was left on the wall in the form of continuous sheets proving that the distances between the tungsten atoms are sufficiently small that their mutual attraction hold them together.

Finally we shall give the results that can be reached in the above mentioned way by the application of a salt layer.

From many experiments we concluded that the mean duration of burning after which the intensity was sunk to 80 % of its original value is for lamps with NaCl about 2,6 times, for lamps with CaF$_2$ 3,3 times as long as for lamps without salt.

Eindhoven. Laboratory of Philips'
Glowlampworks Ltd.

Physics. — *"The ionisation of argon"*. By G. Holst and A. N. Koopmans. (Communicated by Prof. H. Kamerlingh Onnes).

(Communicated in the meeting of December 28, 1918).

1. Franck and Hertz[1]) have pointed out the fact that the conduction of electricity does not take place in the same way in all gases. They divide the gases into two groups: 1st those, in which an electron moving through the gas hardly loses any energy by a non-ionising impact and 2nd gases, in which the energy of the electron is lost for the greater part or totally by each impact. To the first group especially the rare gases belong. Franck and Hertz made themselves a series of measurements with these gases and also gave a theory of the conduction of electricity by them. They principally investigated helium. In the following we shall mention the results of some measurements with argon.

Until now only determinations of Gill and Pidduck[2]) existed on this subject. A former investigation on the spark potential of argon has taught us[3]) however, that the results of these physicists are not quite right, probably by a slight impurity of their argon. This is probably the reason why the typical behaviour of the argon was not pronounced in their measurements.

2. We have again determined the connexion between current and tension in argon. Our apparatus had been constructed in the same way as that of Gill and Pidduck (fig. 1). It consisted of a condensor, in which the variations in the plate-distance could be measured. In the anode a series of holes had been bored through which by means of a quartz lens ultraviolet light of a mercury lamp could be concentrated upon the zinc cathode, in order to liberate electrons from it foto-electrically. By means of a micrometer screw the cathode could be moved up and down. The whole apparatus had been fused into a glass tube with a quartz window to let the ultraviolet light through.

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[1]) Verh. D. phys. Ges. (15), 34, 929, 1913 en (16), 12, 1914.

[2]) Phil. Mag. (16), 280, 1908 en (23), 837, 1912.

[3]) Versl. Kon. Ak. v. Wet. (26), 1027, 1917.

The intensity of the current in the condensor was determined from the time which a binant electrometer of DOLEZALEK needed, to
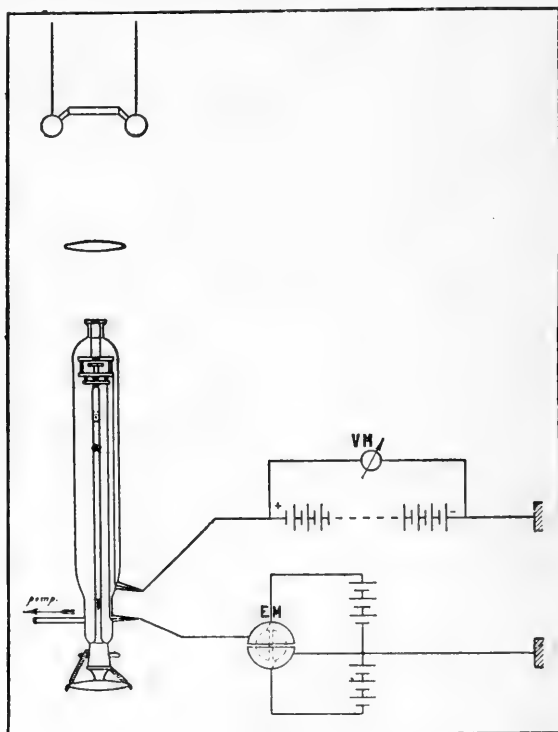
Fig. 1.

be charged. The tension was supplied by a battery of small piles and controlled with an electrometer of WULFF. All conductors, the discharge tube, and the electrometer were protected by tin-foil in order to prevent electro-static disturbances.

The argon was purified according to the method of GEHLHOFF. During the measurement there always was found a small impurity, probably due to gases from the ebonite, by which the condensor was isolated. The pressure increased about by 0.00080 mm. in 24 hours.

The quartz lamp was fed by a battery. After some time the radiation proved to be satisfactorily constant, which was controlled by a thermo-pile.

3. We have made measurements on the relation between current and tension for a constant distance of the condensor plates and on the relation between current and plate distance for a constant intensity of the field.

In fig. 2 and 3 the results of the best measurements have been represented graphically. Both curves show typical sudden changes of

direction due to the augmented increase of the intensity of the
current and which occur at regular distances [1]). For helium
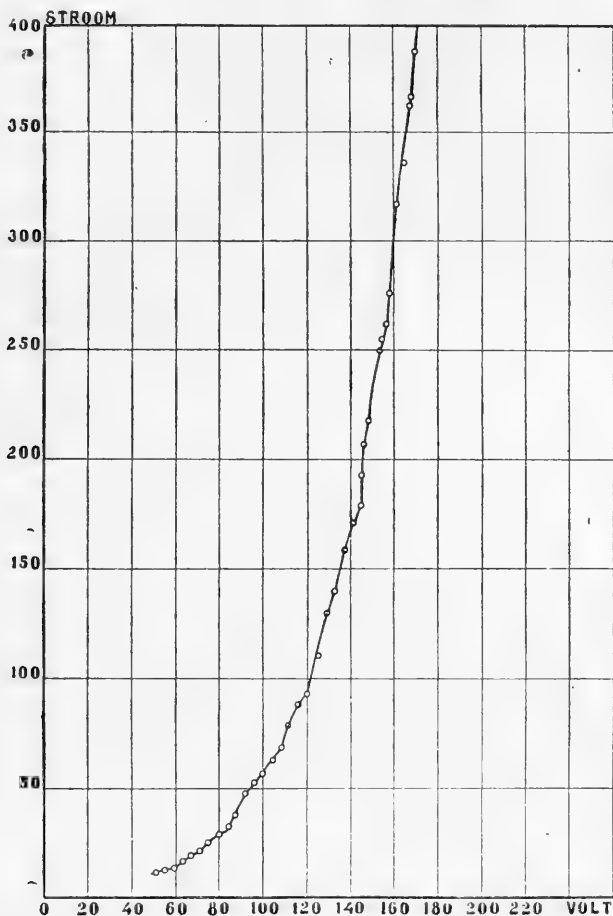
Fig. 2.

FRANCK and HERTZ have observed a similar phenomenon and proved,
that these changes of direction must occur each time an electron has
travelled through a potential difference equal to the ionisation potential.
Our measurements give in this way for the ionisation potential of
argon 12,0 Volt, which agrees satisfactorily with the value FRANCK
and HERTZ found in another way. [2]) In the curve for constant field
the steps are much more pronounced than in that for constant plate

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[1]) Maximally we have observed 15 steps.

[2]) Later measurements by Dr. OOSTERHUIS and one of the writers proved that
no real ionisation occurs at 12 Volts. The real ionising potential is about 17
Volts. So 12 Volts must be considered to be the velocity of first inelastic
impact (Note added in translation).

distance and it seems extremely useful for the precise determination of the ionisation tension. This method has the advantage that it is quite independent of eventually existing contact potentials and besides, that it does not only determine the ionisation tension itself but also a series of multiples of it, so that the mean value can exactly be calculated.

STROOM

150

100

50

1   2   3   4   5 PLAATAFST.IN ¹m/m
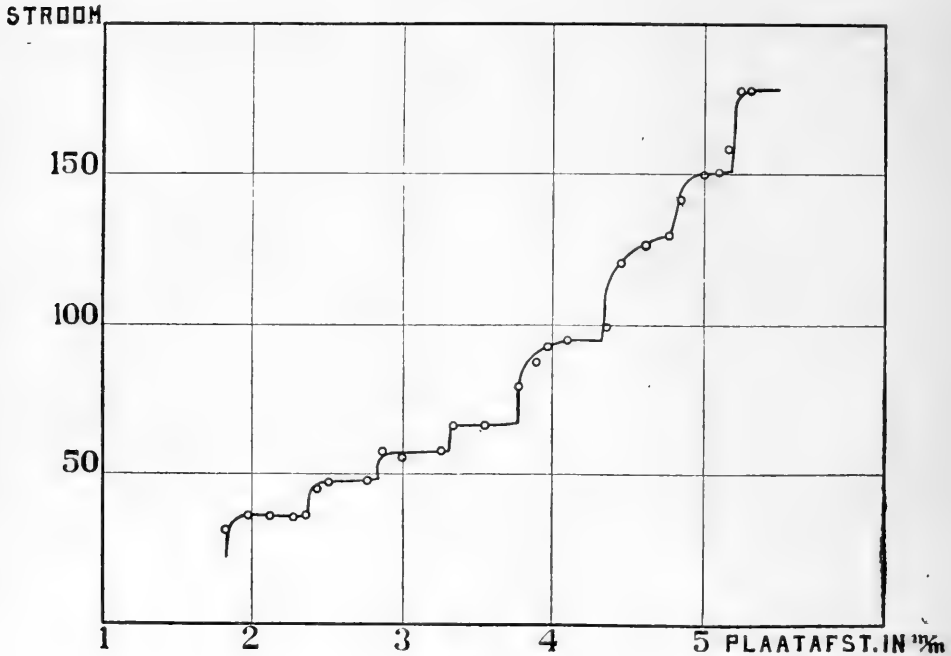
Fig. 3.

4. HERTZ [1]) concluded from the experiment made by him together with FRANCK on helium, that the energy transmitted by an electron to a helium atom at a non-ionising impact has just the value it would have when the impact took place between perfectly elastic spheres with the mass of the electron resp. of the helium atom. Let us suppose now, that also in the argon the impact between an electron and an argon atom follows the law of the elastic impulse. We then find that during a non-ionising impact the electron loses a quantity of energy equal to $V = kE$, where E represents the energy of the electron and k a constant, equal to double the quotient of the mass of the electron by that of the argon atom:

$$k = 2\frac{m_e}{m_a} = \frac{2}{1844.40} = 0{,}000027.$$

Now we can also calculate the increase of the energy of the

[1]) Verh. D. phys. Ges. (19) 268 1917 Verg. BENADE Phys. Rev. (10) ⁷⁷ 1917.

electron between two succeeding impacts. Let v be the velocity of the electron, λ the mean free path, then the mean value of the interval between two succeeding impacts will be $\tau = \dfrac{\lambda}{v}$ sec. During this time the electric field X gives to the electron the acceleration $X\dfrac{e}{m}$. As after each impact the electron begins again with the mean velocity zero in the direction of the electric field, it will travel over a distance $x = \frac{1}{2} X \dfrac{e}{m}\left(\dfrac{\lambda}{v}\right)^2$ in this direction [1]). The mean value of the increase T of the energy between two impacts will therefore be

$$T = Xe\,\tfrac{1}{2}\, X \dfrac{e}{m}\left(\dfrac{\lambda}{v}\right)^2.$$

Evidently this increase becomes smallest when the energy $\frac{1}{2} mv^2$ itself is as great as possible. Then the loss of energy V by the impact is however also maximal and therefore also the ratio $\eta = \dfrac{V}{T}$.

Let us now suppose, what probably will be the case, namely that ionisation will occur, as soon as an electron receives enough energy to be ionised. Then η becomes a maximum for $\frac{1}{2} mv^2 = e\,V_i$, where V_i is written for the ionisation potential

$$\eta_{max} = \dfrac{ke\,V_i}{X^2 e^2 \frac{1}{2}\lambda^2\,\dfrac{1}{mv^2}} = 4k\left(\dfrac{V_i}{\lambda X}\right)^2.$$

Now the free path of an electron in argon is $4\sqrt{2}$ times that of an argon molecule. From the data on internal friction, we can easily deduce, that λ in argon for $17°$ C. and a gas pressure of p mm. is equal to $\lambda = \dfrac{0,028}{p}$ cm.

The ionisation potential for argon is 12 Volt. Introducing this into the above formula we find:

$$\eta_{max} = 20\left(\dfrac{p}{X}\right)^2.$$

In the measurements with constant field p was about 2 mm. and

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[1]) The mean velocity in the direction of the field becomes therefore $v_x = \frac{1}{2} X \dfrac{e}{m} \dfrac{\lambda}{v}$, while HERTZ finds double the value. This must be ascribed to the integration used by H, in which the rare very long paths have a great influence. In reality, when the number of the impacts between two ionising impulses is not exceedingly great, an intermediate value will be the right one.

$X = 250$ Volt$/_{cm}$, so that η_{max} was equal to $\dfrac{1}{750}$. Maximally an electron loses therefore by the impact with an argon atom the $\dfrac{1}{750}$ part of the energy it has gained between two succeeding impacts. In this case the loss of energy may be entirely neglected and we may assume that the energy of an electron it determined only by the way it has travelled in the direction of the field viz. all electrons at the same distance from the cathode will have the same velocity.

In measurements with constant plate distance this is not at all the case. As long as the potential difference between the plates is small, the field is weak and η therefore great. In this case we must therefore always take into account the energy loss by the impacts and especially for the first steps of the current-tension-curve this influence will be considerable. For this reason measurements with a constant practically chosen field are preferable for the determination of the ionisation potential.

As to the height of the steps, according to FRANCK and HERTZ they must be in the ratio $1 : 2 : 4$ etc. When we disregard the round corners the current could be represented as a function of the tension by a formula of the form $i = e N_0 2^n$, where N_0 is written for the number of the electrons emitted by the cathode and n for the greatest integer smaller than $\dfrac{V}{V_i}$. (V is the potential difference between the two plates).

In our measurements the ratio $2 : 1$ never occurred, but $1.3 : 1$ and $1.5 : 1$. Doubtlessly this is due to the influence of impurities in the argon. By these the deviations are also greater in the measurements with a constant field than in those with a constant plate distance. It seems therefore to be of importance to repeat these measurements still with a purer gas. Finally we can conclude from the curves with a constant field, that nearly every impact of an electron that has travelled through 12 Volt causes ionisation. From the preceding calculation it is found, that the mean value of the path travelled by an electron with a velocity corresponding to 12 Volt between two impacts in the direction of the field is 0,001 cm. The measurements teaches however that all ionisations take place in a layer of maximally 0,004 cm., so that nearly each impact that can cause ionisation really does cause it.

Anatomy. — *"Experimental cerebellar-atactic phenomena in diseases lying extra-cerebellar"*. By D. J. Hulshoff Pol. (Communicated by Prof. Winkler).

(Communicated in the meeting of March 23, 1918).

In a previous communication [1]) I pointed out that our equilibrium-organ has not to be exclusively looked for in the vestibular organ as Goltz [2]) writes, and wishes, but that this organ has its arborisations through the whole of the body and that the vestibular apparatus has to be considered only as a subdivision of it.

The equilibrium tracts, which run centripetalwards as tracts of Flechsig and Gower, possess exactly the same function as those fibres of the vestibular apparatus, which too provide for our equilibrium.

Further investigations [3]) then taught me, that sensory cerebellar ataxia must take place, when the above-mentioned afferent tracts in their course through the cerebellum, are damaged.

Should this supposition be true, then from it can be deduced, that cerebellar ataxia can be called forth by interruption of these afferent paths, before they reach the cerebellum.

I therefore put before me the question, whether it should be possible to provoke cerebellar ataxia, 1st by interrupting totally or partially the afferent tracts, which conduct from the medulla spinalis towards the cerebellum, before they reach the corpus restiforme, and 2nd to injure more or less the vestibular nerve, before it arrives within the dura.

In reference to the former, a transsection distally from the restiform body is necessary, because in it also other fibres are found, which do not originate from the medulla spinalis. In reference to the latter, destroying of the vestibular fibres is necessary before they arrive within the scull, because the injuries due to the operation, within the scull, might provoke a matter of complications less wished for.

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[1]) On our equilibrium-organ. Verslag Kon. Akad. v. Wet. Nov. 1917.

[2]) See H. Zwaardemaker, Physiology. II Vol. p 286.

[3]) Cerebellar ataxia as disturbance of the equilibrium sensation. Verslag. Kon Ak. van Wet. Jan. 1918.

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Before starting this experiment in the first place I had to point out, what was meant with cerebellar phenomena.

The gait of the drunkard is, as I made clear in my former report [1]), one of the most striking abnormalities in cerebellar disease. OPPENHEIM on the other hand thought he distinguished still another form of ataxia, which should have a great deal of similarity with spinal ataxia, while DEJERINE thinks under some instances a comparison possible with labyrinthine ataxia. From this follows, that in man no sharply defined disturbances are to be presented as cerebellar symptoms. This can be easily comprehended because with sickly alterations, as tumors of the cerebellum, other symptoms except the local ones are observed.

The pressure of the tumour will manifest itself also on other, far located centra, by which the complex of symptoms, due to the local disease, is no longer sharply delineated.

I therefore soon came to the conclusion that I should not confine myself in my further experiments to the symptoms of the sickbed, but to the results which were obtained by animal investigations.

Here too great care had to be taken, as in reference to the numerous connections of the cerebellum with the other parts of the central nervous system, only those investigations could be of any use, in which exclusively small, well-described parts of the cerebellar surface were taken away.

In correlation of the view of BOLK [2]) I restricted myself in general to the experiments of v. RIJNBERK [3]), in addition to what was found by others.

Putting together in short the obtained results of v. RIJNBERK, one finds: I. ataxia (taken in general) II. ataxia of the head: "no"-nodding; III. gait of the cock, in which the paws are strongly pulled up in the knees. IV. the parade-step, as one sees with the Prussian regiments, and in which the leg is lifted up being stretched forward. V. turning around the long-axis of the body. VI. pleuro-tatonus or bending of the trunk towards the left or towards the right.

If I add to these still one single symptom from my own experi-

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[1]) Cerebellar ataxia as disturbance of the equilibrium sensation. Verslag Kon. Ak. v. Wet. Jan. 1918.

[2]) BOLK, Principal features of the comparative anatomy of the cerebellum of the mammals, particularly in correlation of the structure of the cerebellum in man. Psych. en Neurolog. bl. 1902.

BOLK, On the physiological significance of the cerebellum. Haarlem. Erven Bohn. 1903.

[3]) G. v. RIJNBERK, On functional localisation in the cerebellum. Verh. Bataafsch Gen. 1906.

ments [1]), then it is the following. VII: swaying movement of the body, with the coxa as resting-point.

The animal sits on its hind part, while the front part, resting on the fore legs, constantly tosses to the right or to the left, exactly as the pendulum of a clock. This movement is, as I suppose, the same as described in sub II, although more intensified, because not only the head, but nearly the whole of the body participates in it.

As all these symptoms were never found in one and the same animal experimented on, but changed according to the parts which were excochleated, and totally in accordance with the view of BOLK, I supposed that in the new experiments some of them would come to the foreground.

The aim of the operation [2]) therefore was to leave only unsectioned a part of the afferent cerebellar tracts. For this purpose the connections between the medulla spinalis and the cerebellum were to be sectioned in first instance, and as soon as the animal should have overcome the disturbances of gait, resulting from it and thus walked well again, then the vestibular apparatus was destroyed *unilaterally*.

By this method still some afferent tracts should reach the cerebellum and in this way a partial lesion of its cortex should be imitated.

Referring to the first part of the experimental operation, we know, that from the funiculi posteriores, through the interposition of the nuclei of GOLL and BURDACH, stimuli still reach the restiform body and the cerebellum along the fibrae arcuatae ext. post. et anter. It should be of importance not only to section the spino-cerebellar tracts, but also the funicular posterior tracts.

The ideal place for this would be above the I[st] cervical root, because there all the medullary fibres going to the cerebellum can be sectioned. The endeavours applied for this purpose failed however, as all the cats died during the operations. Therefore I resolved to perform the section on a lower level, i.e. between c_2 and c_3. For this purpose the dorsal part of the secund arcus vertebrae cervicalis was cut off, the dura was opened and between c_2 and c_3 in the first place both the posterior funiculi were transsectioned and later on with a small curved knife the lateral edge of the medulla was cut in. By microscopical examination it was stated, that it had not

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[1]) Cerebellar ataxia Experimental reseaches. Psych. Neurol. Bl. 1909.
Cerebellar functions in correlation of their localisation. Id. 1915.

[2]) Prof. B. MAGNUS and his temporary substitute Dr. W. STORM VAN LEEUWEN, had the kindness to let me operate in the pharmacological laboratory, for which opportunity I am greatly indebted to them.

been possible to quite spare the pyramidal tract, which could be easily observed in the animals. During the first days after the operation the walking took place with great difficulty. The animal not only was ataxic, but more or less paralysed, often falling aside. Within 10 or 14 days however it had recovered in so far, that it could walk in a straight direction. When it had almost totally recovered, then I passed on to the second operation, and through the right bulla ossea, according to the method of DE KLEYN[1]), the labyrinth and the vestibular nerve were destroyed.

In five cats the operation succeeded as we wished it. The symptoms they showed were in general the following:

a. After transsection, on the right as well as on the left of the posterior funicular tracts and of the spino-cerebellar tracts, ataxia and paralysis resulted, as mentioned above. That ataxia occurs after transsection of the tracts of FLECHSIG and GOWER was already known to us from the investigations of MARBURG and BING.[2]) The palsies were the results of a not wanted lesion of the lateral pyramidal tracts when transsectioning the spino-cerebellar lateral tracts. After a fortnight these symptoms diminished, the animals could walk rather well in a straight direction and then I went on to the second operation, destroying this time the vestibular organ and the fibres originating from it.

b. After the *right* labyrinth was destroyed and when the animals awakened from the narcosis, they showed in most of the cases all the symptoms, known and found as result of the operation. Always to be observed were eye-nystagmus towards the *sound* side, on the other hand, retraction of the third eye-lid, narrow pupil and narrow eye-slit (trias of sympathetic palsy, DE KLEIN and SOCIN[3])) on the *sick* side. Nystagmus of the head I never observed, however I saw turning of the head towards the *operated* side. In some cases this turning was distinctly, in other cases less distinctly visible.

c. Soon after the operation the animals exhibited a more or less marked circus gait towards the *sound* side, i.e. towards the *left*. Several degrees of this deviation were observed. In the most pronounced cases the animal rotated as it were around its tail. When the circus gait was not distinctly pronounced, then the animal walked

[1]) A. DE KLEYN, Zur Technik der Labyrinthextirpation und Labyrinthausschaltung bei Katzen. Archiv. f. die Ges. Phys. Bd. 145.

[2]) See EDINGER, Zeitschr. f. Nerv. Heilk. Bd. 45. 1912. bl 303.

[3]) A. DE KLEYN u. CH. SOCIN, Zur näheren Kenntnis des Verlaufs der postganglionären Sympathicus-bahnen für Pupillenerweiterung, Lidspalt-eröffnung und Nickhautretraktion bei der Katze. Archiv f. d. Ges. Phys. Bd. 160. 1915.

in a more or less large circle constantly towards the sound side. When the deviation occurred in a slight degree, then the animal only showed a deviation of its gait directed to the sound side.

The cause of these differences I think I may find in the incompleteness of the operations. When these succeed according our wish, then the deviation will be very distinct. When the operation falls out less well, then the circus gait too will not come to full development.

As is the case with most of this kind of operations, the deviation soon grew less and compensation therefore soon appeared. The distinctly marked circus gait changed into a curved line walk and ended towards a walk deviating to the sound side. This last symptom remained during a long time.

Yet the animal could manage, although the circus gait was distinctly pronounced, to reach a certain point. As it however was inclined to deviate towards the sound side, it was obliged to try this in a particular way. This is clearly seen from the drawing after a photograph (figure 1) of a gait line. The animal is standing near A and intends to go to B, where a piece of meat is lying. As it is inclined to deviate towards the *left*, the sound side, and in this way would never reach its aim, it adducts its *right* hind leg strongly underneath its trunk and when the *left* hind leg then is lifted, the animals throws, by means of the strongly adducted *right* hind leg, the whole of the hind trunk towards the *left*, and therefore the head becomes directed more to the right, towards the aim. This is distinctly seen, just above the arrow, which indicates the intended direction of movement. $I.$ notes the place where the R fore leg is placed. The R hind leg is strongly adducted underneath the trunk towards $II.$ As it, with that leg, throws the whole of its hind trunk towards the left, then the long-axis of the trunk is indicated by drawing a line between the two right legs, therefore $I.$ and $II.$, in which case the animal keeps looking at the aim. With the next step the R fore leg is placed near $I..$ and the R hind leg is strongly adducted, towards $II..$ The long axis is found between $I..$ and $II..$, and therefore the head is again turned towards B. Continuing in this way, thus adducting the right hind leg strongly underneath the trunk, the animal at length reaches its aim along a curved line. It happens now and then that the cat, when adducting the R hind leg too much underneath the trunk, loses its equilibrium and tumbles to the *right*, because it misses its support on that side of its hind trunk.

Moreover it is remarkable that when the cat walks aimlessly

about the room, it constantly turns towards the wall, against which

Fig. 1.

it rests the *sound left* side and along which it moves on. This
way of doing is comprehensible, because by leaning on the *left* side

against the wall, it cannot deviate in that direction and in this manner the straight line of gait along the wall becomes easier.

_d._ When we examine the gait of these cats carefully, we directly see that the fore leg is stretched and lifted high. On the following picture (fig. 2), a high magnification after a film reproduction, this is clearly seen. Without much difficulty one recognises the parade-step, as i.a. is published by Luciani and v. Rijnberk in their investigation on the cerebellum. From my own experiments[1]) on dogs, of which a reproduction (fig. 3) is placed next the cat's, and which is made of a photograph, one sees the confirmation plainly.

Fig. 2.
Cat. extra-cerebellar.
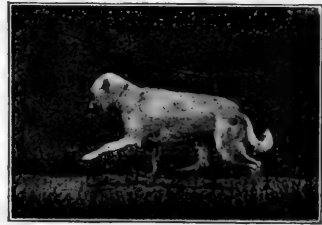
Fig. 3.
Dog, intra-cerebellar.

Of importance is the fact that in the dog the parade step occurred after operating _in_ the cerebellum (fig. 3), that in the cat, after operating _extra_-cerebellar (fig. 2).

Other symptoms important for this report are not found in the operated cats. _Yet the results which we obtained, support the supposition that the sensory cerebellar ataxia occurs, when the afferent tracts, which from the medulla and the vestibular organ pass on towards th. cerebellum, during their course to that organ, are interrupted in some way or other._

In connection with the above-said a few points still rest to be spoken of:

1. how can it be explained that in my extra-cerebellar operation, the parade step was perceived, while on the other hand the cock-step and the "no"-nodding etc. as described by e.g. Luciani, v. Rijnberk and myself were missing.

I think I must look for the reason that in all these cases the same operation always was done, i.e. transsection of the posterior funiculi medullae, of the ventral and dorsal spino-cerebellar tracts of the funiculus lateralis medullae and of the vestibular organ at

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[1]) Cerebellair ataxia Psych. Neurol. bl. 1909.

the *R* side. Perhaps other cerebellar symptoms would have come more to the fore-ground when a different combination had been made.

II. In my previous report[1]) I came to the conclusion that, as sensory cerebellar ataxia must arise through interruption of the afferent, extero- and proprioceptive equilibrium tracts in the cerebellum, this ataxia naturally will appear, when *those* parts of the cerebellum are affected, where these fibres are found.

The consequence is that where the parade-step can be evoked *extra*-cerebellar, and this symptom also is derived *intra*-cerebellar, a field of the cortex must be destroyed in which these afferent fibres end.

Now it is well-known that the tractus spino-cerebellaris dorsalis (FLECHSIG) ends in the cortex of the vermis, and the tractus spino-cerebellaris ventralis (GOWER) in the vermis superior and the nuclei tecti. From this follows, that all the important afferent tracts from the medulla spinalis and from the vestibular organ are only in connection with the vermis and the above mentioned nuclei.

Previous experiments[2]) which I made proved however, that the paradestep appears after removal of parts of the cortex of the lob. paramedianus, lying laterally from the vermis.

These two facts therefore do not agree and the question arises, whether an explanation is to be found for this. Directly three possibilities come to the fore ground. The *first* is that my investigations were not properly made. Against this I would say, that in ten dogs, larger and smaller parts from the lobulus paramedianus were cut out and that in seven dogs the parade-step was found, while this dysmetria in the gait did not appear in any of my other animals. Therefore it is likely, that the right localisation was obtained.

The *second* is, that the view is not right, that the mentioned afferent tracts should only end in the vermis, but that they possibly also pass into more laterally lying parts of the cortex. Against this can be advanced, that a great number of investigators have proved, that the mentioned tracts do not end outside the vermis. This fact too may be taken for certain.

The *third* explanation could be, that one has in the cerebellum correlations, which histologically are not yet brought to clearness and through which the afferent impulses, arrived at the vermis, are projected towards other parts of the cerebellum.

In this report I will not go deeper into the last question, which to me seems the most probable, as more special investigations will

[1]) Verslag Kon. Akad. v. Wet. Januari 1918.

[2]) Psych. Neurol. bl. 1909.

right. *Proximally* degeneration appears of the posterior funicular tracts, the spino-cerebellar lateral funicular tracts and the spino thalamic tract. This afferent degeneration too is far more visible on the right than on the left side. Of the spino-cerebellar tracts, the dorsal is the most affected, the ventral (GOWER) less. At the right the nervus vestibularis degenerated.

Cat No. 2. Operation done as in N^0. 1. After the animal awakened from the aether narcosis, it did not show signs that the right vestibular organ was destroyed. Next day the operation was repeated, then with satisfactory result. Noted were 1. Eye-nystagmus to the *left*. 2. Sympathetic palsy trias at the *right*. 3. No head-nystagmus 4. No, or very little turning of the head.

The day after the operation the cat walked rather well, it hardly showed circus gait, but only had an inclination to deviate to the *left*, hence to the sound side.

Eight days after the operation of the vestibular organ the cat was killed for examination. This investigation too Prof. WINKLER had the kindness to make; the following was found by him : Caudally from the field of operation lying between c_2 and c_3 there is found a rather strong degeneration of the pyramidal lateral funicular tract, but contrary to cat N^0. 1, there were but few black spots in the tecto-spinal region. Capitalwards the posterior funiculi are degenerated and of the spino-cerebellar lateral funicular tracts principally the FLECHSIG, i.e. the dorsal, bundles. Moreover one sees an afferent degeneration within a group of fibres, which originate from the dorsal part of the spino-cerebellar lateral funicular tract of FLECHSIG. They take their course medialwards, break through the zona inter-media, cross in the commissura alba ventralis and take a place in the sulco-marginal region. In following this bundle upwards, it is seen capitalwards of the decussatio pyramidalis against the ventral margin, laterally from the pyramidal tracts. Higher still it is found in the lemniscus in the place, where the spino-thalamic tract lies. As the slides do not reach the thalamus, I could not make out where this bundle ended. All the above mentioned symptoms are more distinctly pronounced on the right than on the left, except of course of the crossed part of the last mentioned bundle. The vestibular nerve is degenerated at the right side.

Cat No. 3. Operation as with N^1. 1.

After awakening from the aether narcosis there existed I. eye nystagmus to the sound side; II. sympathetic palsy trias to the right; III. turning of the head to the right; IV. no head nystagmus. The day after the operation circus gait to the left appeared, i.e. to the sound side, but this was not half so distinctly pronounced as with cat N^1. 1. As was the case with cat N^0. 1, here too the circus gait soon diminished, yet for weeks the animal showed still an inclination to deviate to the left. Also the curved line of gait to reach an object (fig. 1) remained, although this was not so distinctly visible as in the beginning.

From a film exposition it proved, that the parade step was distinctly present.

As the cat already previously had been used for another cerebellar operation, the central nervous system was not examined, as the obtained results might have been influenced by it.

Cat No. 4. Instead of transsectioning on both the sides of the afferent medullary tracts to the cerebellum, in this cat only the right half was transsectioned. After the animal had totally recovered from the operation, the vestibular organ and the vestibular nerve, as in the three previous cats, were destroyed at the right side.

After awakening from the aether narcosis the same symptoms were observed as with the other cats, thus I. nystagmus to the left, II. sympathetic palsy trias to the right, III. turning of the head to the right, IV. no head-nystagmus.

The day after the operation the animal did not show many symptoms. After the second day there was circus gait to the left. On the fourth day this last was still visible and a film exposition was taken. The parade step appeared then distinctly visible.

On the sixth day a change in the cat appeared. The animal tumbled over regularly to the right, it could not walk and mewed strongly. On the seventh day the cat lay dead in the cage, after more than 20 days after the operation in the medulla spinalis was done. For the section see cat N'. 5.

Cat No. 5. Operation as with N⁰. 4.

After awakening from the aether narcosis this cat too showed exactly the same symptoms as the former cats, only the circus gait was not so distinct as with cat N⁰. 4. The further course was nearly the same. After film-exposition the parade step appeared distinctly to be present (fig. 2). As with N⁰. 4, this cat too was found dead in its cage, nearly at the same time and three weeks after the operation, done in the medulla spinalis, but without the symptoms which N⁰. 4 had exhibited shortly before dying.

The section by a mishap was only done on the head, as this was cut from the trunk and was kept in formaline, while the body was thrown away. After opening of the crane, the bloodvessels of the brain surface and of the spinal cord up to the place of operation were strongly overfilled. The wound itself was well-cured, the candally lying part did not show alterations. After microscopic examination an infiltration of small cells was found underneath the pia As this alteration appeared three weeks after the operation and as both the cats were placed in one cage and died nearly at the same time, the possibility exists, that they died of a general infection.

Chemistry. — "*The Phenomenon Electrical Supertension*". II. By
Prof. A. Smits. (Communicated by Prof. P. Zeeman).

In the first communication on the phenomenon of electrical super-
tension the supertension of the hydrogen etc. has been considered
which appears at unattackable electrodes on the passage of an
electric current. Now we shall discuss the phenomenon of super-
tension at the generation of hydrogen, which occurs when metals
act on water, or on solutions of acids without the aid of an electric
current, i.e. *without entrance of electrons from outside.*

In the discussion of the hydrogen generation on immersion of
zinc in an acid zinc salt solution the adjoined figure 1 led us to
make the following remarks.

When zinc $(M^{\cdot\cdot})$ is placed in a liquid of the concentration x_1,
the zinc can be electromotively in equilibrium with this solution,
but only metastable, at an electrical potential indicated by the dotted
line gf.

In this case no hydrogen-generation should, however, take place.

The metal zinc does act, however, on the here supposed liquid,
and hydrogen is generated, which gives rise to a *three-phase equili-
brium*, consisting of a hydrogen-containing metal phase, a hydrogen
phase, and the electrolyte, in which we should bear in mind that
by what is here indicated as electrolyte, the liquid phase in the
boundary layer is meant. On action of the metal on the electrolyte
the concentration of the liquid in the boundary layer will differ
from that of the liquid outside the boundary layer.

In consequence of the reactions

$$
\begin{array}{ccc}
M_s \rightarrow M_s^{\cdot\cdot} & + & 2\theta_s \\
\downarrow \quad \downarrow & & \downarrow \\
M_L \rightarrow M_L^{\cdot\cdot} & + & 2\theta_L \\
& & \downarrow \\
& 2\theta_L + 2H_L^{\cdot} \rightarrow H_{2L} \\
& \downarrow \qquad \downarrow \qquad \downarrow \\
& 2\theta_G + 2H_G^{\cdot} \rightarrow H_{2G}
\end{array}
$$
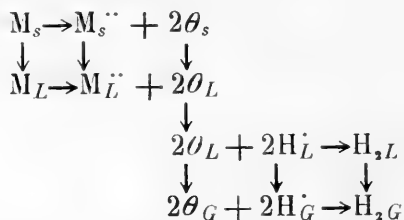
the liquid in the boundary layer will be poorer in hydrogen-ions
and richer in zinc-ions than the electrolyte outside the boundary
layer.

When now also on rapid solution the metal assumes internal
equilibrium superficially, the metal phase will lie on *ad* or on the
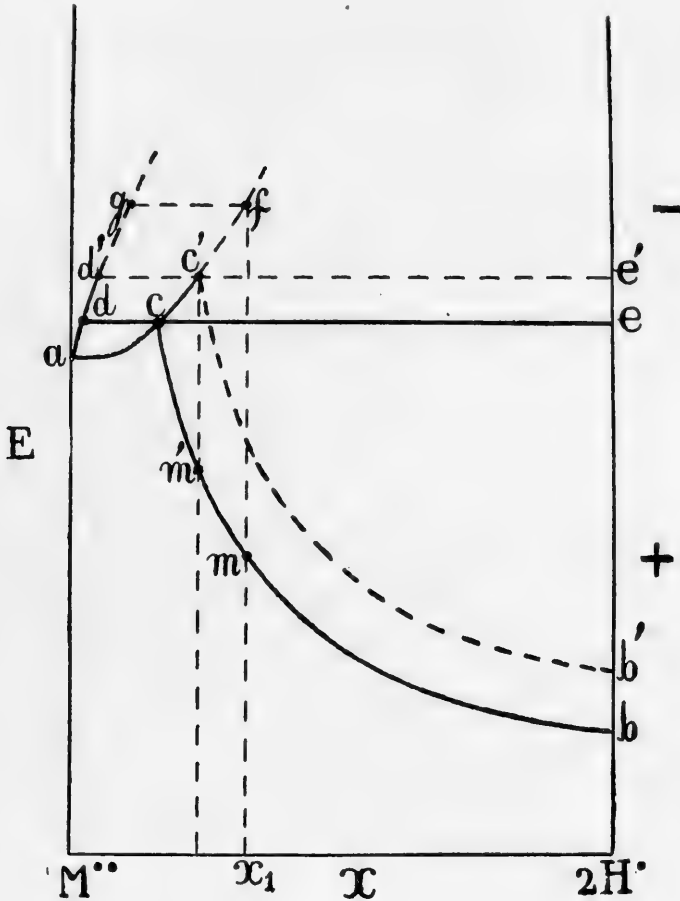
Fig 1

prolongation of this line, because the different points of this curve
and its prolongation represent states of internal equilibrium of the
metal in electromotive equilibrium with electrolytes which lie on
the line *ac* or its prolongation.

When not only the metal phase, but also the hydrogen phase of
the three-phase equilibrium mentioned just now is in internal equili-
brium, the metal phase must lie in *d*, the hydrogen phase in *e*, and
the electrolyte in the boundary layer in *c*, the electrolyte outside
the boundary layer possessing the concentration x_1. The zinc-ions
will, therefore, continually diffuse from the boundary layer outwards,

and the hydrogen ions in opposite direction from outside into the boundary layer.

Let us now first of all suppose that the internal equilibrium in the metal sets in very rapidly, but not in the hydrogen. This may take place when the metal maintains its internal equilibrium also on rapid emission of ions and electrons, and the internal equilibrium:

$$2\theta + 2H \rightleftarrows H_2$$

does not set in rapidly enough, so that a gas-phase escapes which contains too many electrically charged particles, i.e. too many ions and electrons or in other words is disturbed in *base direction*. In this case the three-phase equilibrium: metal phase – boundary liquid – hydrogen phase will be indicated by e. g. the three points $d'c'e'$.

When the electrical potential of the same disturbed hydrogen phase could be measured with regard to the electrolytes of other hydrogen-ion concentrations than c', the line $b'c'$ would denote the electrolytes which can coexist with the same disturbed hydrogen for different electrical potentials.

We shall now consider the case that the internal equilibrium sets

Fig 2

in very rapidly for the hydrogen, but that the metal is disturbed. It being supposed here that the metal dissolves pretty rapidly, the liquid in the boundary layer will deviate also here from that outside the boundary layer with the concentration x_1. The hydrogen phase is in internal equilibrium, so that the coexisting liquid must be a point of the line bc. The disturbed metal phase is ennobled, and has, therefore, a less negative electrical potential. Let this metal phase be indicated by d', then the three coexisting phases are represented by the points $d'c'e'$, and the line $a'c'$ has only significance for the case that the same disturbed metal phase could also coexist with other electrolytes than c'.

A third possibility remains, namely this that neither the metal phase nor the gas phase assume internal equilibrium with sufficient rapidity. In this case the metal will, therefore, contain too few ions and electrons, in consequence of which its electrical potential has become less negative, whereas the hydrogen phase contains too many ions and electrons, from which results that its potential has obtained a more negative value.

Fig. 3

In this case the metal has, accordingly, become *ennobled*, but the hydrogen has become *baser*.

It is now the question at what potential the three-phase equilibrium will lie.

When the disturbance of the metal is much greater than that of the hydrogen, the three-phase potential will most probably be less negative than in case of internal equilibrium of metal and hydrogen phase; if, however, the disturbance of the hydrogen is very great, it is possible that this disturbance prevails, and that the three-phase potential is more negative than in case of internal equilibrium. In the foregoing diagram, fig. 3, the former is supposed.

It is clear how on these considerations we are gradually led to the case that presents itself for Nickel.

There the metal is disturbed, and through its exceedingly slow, imperceptible generation the hydrogen is always in internal equili-

Fig 4
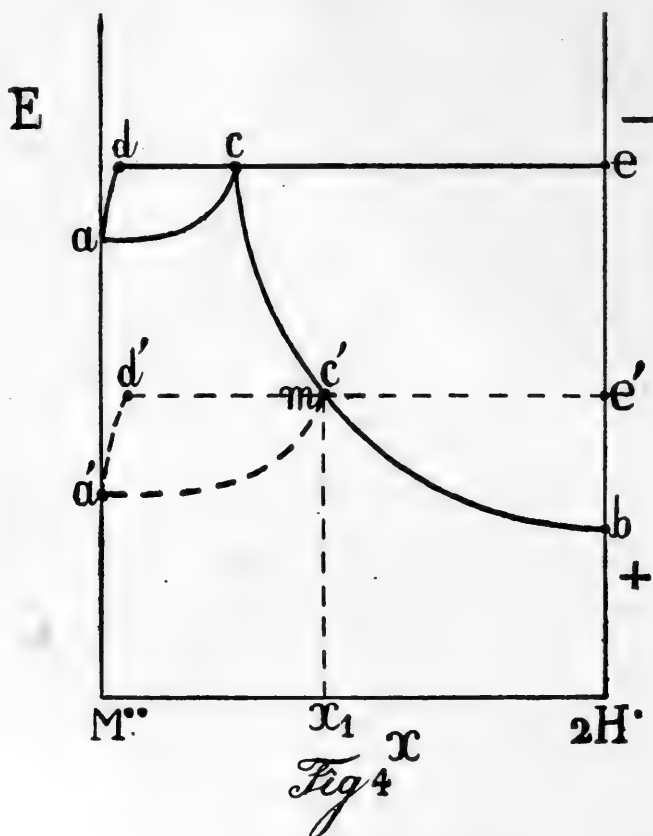
brium. In consequence of the exceedingly slight action the concentration of the boundary liquid is practically not different from that outside the boundary layer, so that the liquid phase of the three-

phase equilibrium will be indicated by the point m, so that the three-phase potential coincides with the potential of the hydrogen electrode, as was already demonstrated before.

Now it is perfectly clear from the considerations given here that we are not justified in saying that when the hydrogen generates at a metal of a potential which is baser than that of the hydrogen electrode, the hydrogen presents the phenomenon of supertension. Fig. 2 e.g. refers to this case, here the generated hydrogen shows no supertension, because the liquid lies in the boundary layer on the line bc. The point c' lies, indeed, above m, but this is only owing to this that in consequence of the solution of the metal, the concentration of the liquid, in the boundary layer, is different from that outside it.

In the cases represented by figures 1 and 3 the hydrogen presents supertension, but this supertension is not equal to the potential difference between the potential of the generating hydrogen and the hydrogen electrode, for in order to get to know the supertension it would be necessary to have the hydrogen electrode also in the boundary layer of the dissolving metal.

The real supertension can be read from the figures 1 and 3 mentioned, it is not the distance from the point m to the horizontal line $d'e'$, but equal to the distance $m'c'$.

Laboratory of Anorg. and General Chemistry of the University.

Amsterdam, January 20th, 1919.

Physics. — *"Contribution to the theory of adiabatic invariants."* (Preliminary communication). [1]) By G. KRUTKOW. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of Dec. 29, 1918).

Introduction. Any quantity that has to be quanticized, which may be called a "quantum-quantity", must satisfy two conditions:

1. it must be a function of the integrals of the equations of motion of the system under consideration. This condition is self-evident, since the quantity must not change by the motion of the system, and has therefore never been explicitly stated;

2. it must be an adiabatic invariant, i. e. it must not change when the system is submitted to a reversible adiabatic influence. This demand was first formulated by EHRENFEST and proved by means of general statistical reasoning [2]). Assuming that the adiabatic influence may be calculated by the methods of mechanism this condition follows directly from the fact, that the quantum-quantity varies abruptly, whereas the external influence may be infinitely small; the quanticizable quantity therefore cannot vary at all, it must be an adiabatic invariant.

Calling the quantum-quantity v, the integrals of the equations of motion $c_1, c_2 \ldots$ and the adiabatic invariants $v_1, v_2 \ldots$ the conditions (1) and (2) are expressed by

$$v = funct\,(c_1, c_2, \ldots.) \qquad \ldots \ldots \ldots \quad (1)$$
$$v = funct\,(v_1, v_2, \ldots.) \qquad \ldots \ldots \ldots \quad (2)$$

3. There is still another condition which a quantum-quantity has to satisfy: it must have a meaning which is independent of the system of co-ordinates. This condition appears to me to embody the notion of the coherence of the degrees of freedom established by PLANCK [3]). To this condition I hope to be able to return in a later

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[1]) Address delivered in the Petrograd. Phys. Ges. in Dec. 1917 and April 1918.
[2]) P. EHRENFEST. Ann. d. Phys. 51 (1916) p. 327, Phys. Zschr. (1914) p. Acad. Amsterdam 22 (1913) p. 586. Ann. d. Phys. 36 (1911) p. 98. Verh. d. D. phys. Ges. 15 (1913) p. 451.
[3]) M. PLANCK. Ann d. Phys. 50 (1916) p. 285.

paper: on this occasion it will be left out of account and we shall only deal with condition (2).

This condition imposes on us the task to find the adiabatic invariants of a given mechanical system and to look for a general method of solving the "adiabatic" problem.[1] A method of that kind was unknown so far; the adiabatic invariants had to be guessed at and their adiabatic invariability had to be tested a posteriori. In this way the following invariants were found:

a. the quantity V of statistical mechanics, which measures the phase-extension limited by the "energy-surface"[2];

b. the "action" calculated for a full period of a periodical system;

$$v = \int_{\tau} 2\, T\, dt\,[3];$$

c. the quantum integrals of the "conditionally periodic" systems;

$$v_i = \int_0^{b_i} p_i\, dq_i = 2 \int_{a_i}^{b_i} p_i\, dq_i .\,[4]$$

In what follows I shall sketch out a general method of finding adiabatic invariants and apply it to certain special cases, viz.

α. Cyclic systems. Properly speaking these systems come under the head of conditionally periodic systems; but as the conditions are particularly simple in this case and bring out the very natural character of the method, I shall discuss them separately;

β. conditionally periodic systems;

γ. ergodic systems.

Under (β) I shall only consider the limiting case, in which there are no commensurable relations between the periodicity-moduli. To the further cases and in particular their relation to the third condition stated above I hope to return on a later occasion.

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[1] This point was specially emphasized by EHRENFEST. Compare for instance P. EHRENFEST Phil. Mag. VI Vol. 33. p. 513 (1917).

[2] P. HERTZ. Ann. d. Phys. 33 (1910) p. 544.

[3] L. BOLTZMANN. Prinz. d. Mechanik II p. 181. P. EHRENFEST Ann. d. Phys. 51 (1916) p. 327 Anhang.

[4] J. M. BURGERS. Ann. d. Phys. 52 (1917) p. 195. To the papers in the Proceedings of the Amst. Acad. referred to by the author I had unfortunately no access.

The general method.

1. *Definition of adiabatic invariants* [1]). We consider a mechanical system of n degrees of freedom, the equations of motion of which must be written in the Hamiltonian form

$$\dot{p_i} = -\frac{\partial H}{\partial q_i}, \quad \dot{q_2} = \frac{\partial H}{\partial p_i}, \quad (i = 1, 2, \ldots, n) \quad \ldots \quad (3)$$

H is here a function of the p_i and q_i. It must not contain t explicitly. Moreover it is supposed to depend on certain external co-ordinates, which we shall call the parameters a_x. These parameters may either retain constant values, in this case we have the iso-parametric problem, or they may vary, which gives the rheo-para-metric problem, or they may vary very slowly [2]), which is the herpo-parametric or adiabatic problem, to which we shall give special attention.

We shall make the following assumptions:

I. None of the quantities p_i or q_i increases to infinity. The q_i are confixed within fixed limits.

II. During the time in which each q_i goes to and fro many times between its extreme values, the a_x must change by an infinitely small amount of the first order. Moreover each $\dot{a}_x$ must be approximately constant. Equations (3) must remain valid during the process. It follows from these assumptions that the herpo-parametric problem, will be obtained by putting $\dot{a}_x = const.$ in the rheo-parametric problem and then taking for all the quantities the time-average in the corresponding iso-parametric problem.

In our discussion we shall confine ourselves to one parameter a. This is not an essential limitation of the problem, but it simplifies the formulae considerably.

An adiabatic invariant is a function v of the integrationconstants $c_1, c_2, \ldots$ of the iso-parametric motion and of the parameter a, the total "adiabatic" derivative of which with respect to a disappears:

$$\overline{\frac{dv}{da}} = \frac{\partial v}{\partial a} + \frac{\partial v}{\partial c_1}\overline{\frac{dc_1}{da}} + \frac{\partial v}{\partial c_2}\overline{\frac{dc_2}{da}} + \cdots \quad \ldots \quad (4)$$

where the horizontal line indicates the time-average.

2. *The iso-parametric problem.* In the equations of motion (3) we

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[1]) Comp. P. EHRENFEST l. c. and J. M. BURGERS l. c.

[2]) Implicitly this condition will show itself in the fact, that HAMILTON's function only contains the parameters a_x itself and not the corresponding moments.

put $a = $ const. and integrate according to JACOBI's method. If

$$H_1 = c_1, H_2 = c_2, \ldots H_n = c_n \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

is a set of normal integrals of the equations, from which p_i may be solved, the characteristic function

$$V = \int \sum_i F_i \, dq_i, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

may be formed, where the functions $F(q_i, c_i, a)$ represent the quantities p_i deduced from equations (5), and putting

$$\frac{\partial V}{\partial c_1} = t_1 \qquad \frac{\partial V}{\partial c_2} = t_2 \quad \ldots \quad \frac{\partial V}{\partial c_n} = t_n \quad . \quad . \quad . \quad . \quad (7)$$

these will be the additional integrals, where

$$t_1 = t + c_1{}^* \quad t_2 = c_2{}^* \quad \ldots t_n = c_n{}^* \quad . \quad . \quad . \quad . \quad (8)$$

The quantities $c_i{}^*$ are the n integration-constants. The iso-parametric problem is thereby solved.

3. *The differential equations of the rheo-parametric problem.* In order to obtain these equations we shall pass from the variable quantities p_i and q_i to the variables c_i and t_i. This is a "contact-transformation". It is obtained by means of the characteristic function

$$V(q_i, c_i, a) = \int \sum_i F_i \, dq_i \quad . \quad . \quad . \quad . \quad . \quad . \quad (6')$$

as transformation-function

$$\frac{\partial V}{\partial q_i} = p_i \qquad \frac{\partial V}{\partial c_i} = t_i \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The differential equations retain the Hamiltonian form. If a remains constant, the new Hamiltonian function is equal to the transformed old one, i.e. to c_i and the following trivial result is obtained:

$$\dot{c}_1 = 0, \dot{c}_2 = 0, \ldots \dot{c}_n = 0 ; \dot{t}_1 = 1, \dot{t}_2 = 0, \ldots \dot{t}_n = 0$$

We now allow a to change, i.e. we put $a = $ function (t). The transformation-function V is now an implicit function of t through the intermediary of q_i, c_i and a:

$$\frac{\partial V}{\partial t} = \sum_i \left(\frac{\partial V}{\partial q_i} \dot{q}_i + \frac{\partial V}{\partial c_i} \dot{c}_i \right) + \frac{\partial V}{\partial a} \dot{a}$$

The differential equations (3) retain their form all the time, but the new Hamiltonian function K now becomes

$$K = c_1 + \left(\frac{\partial V}{\partial a} \right) \dot{a} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where the brackets are intended to indicate, that the derivative $\partial V/\partial a$ must be expressed in the variables c_t and t_t. The differential equations of the rheo-parametric problem therefore are as follows:

$$\dot{c}_1 = -\frac{\partial K}{\partial t_1} \quad \dot{c}_2 = -\frac{\partial K}{\partial t_2} \cdots \dot{c}_n = -\frac{\partial K}{\partial \cdot_n} \left.\begin{matrix} \\ \\ \\ \\ \end{matrix}\right\}$$

$$\dot{t}_1 = \frac{\partial K}{\partial c_1} \quad \dot{t}_2 = \frac{\partial K}{\partial c_2} \cdots \dot{t}_n = \frac{\partial K}{\partial c_n} \qquad (11)$$

4. The herpo-parametric or adiabatic problem.

To begin with we put $a = \mathrm{const.}$ Substituting the value of K from (10) the equations (11) then assume the form:

$$\dot{c}_i = -a \frac{\partial}{\partial t_i}\left(\frac{\partial V}{\partial a}\right) \qquad\qquad (i = 1, 2, \ldots u) \left.\begin{matrix} \\ \\ \\ \\ \end{matrix}\right\}$$

$$\dot{t}_1 = a \frac{\partial}{\partial c_i}\left(\frac{\partial V}{\partial a}\right) + 1 \qquad \dot{t}_x = a \frac{\partial}{\partial c_x}\left(\frac{\partial V}{\partial a}\right) \quad (x = 2, 3, \ldots n) \qquad (12)$$

or, indicating the differentiation with respect to the parameter a by means of a dash:

$$c'_i = -\frac{\partial}{\partial t_i}\left(\frac{\partial V}{\partial a}\right) \qquad t'_1 = \left(\frac{\partial V}{\partial a}\right) + \frac{1}{a} \qquad t'_x = \frac{\partial}{\partial c_x}\left(\frac{\partial V}{\partial a}\right) \quad . \quad . \quad (12')$$

We now only need to put the line which indicates the mean value on the left side and on the right actually to calculate the time-average in order to obtain the differential equations of the herpo-parametric or adiabatic problem. The integration, in which the said line on the left is omitted, gives the adiabatic invariants; indeed, the equations being

$$c'_i = f_i(c_i, t_i, a) \qquad t'_i = g_i(c_i, t_i, a)$$

and $\varphi(c_2, t_2, a)$ their integrals, the total differential $d\varphi/da$ owing to the equations must disappear, or

$$\frac{d\varphi}{da}\frac{\partial\varphi}{\partial a} + \sum_i \left(\frac{\partial\varphi}{\partial c_i}f_i + \frac{\partial\varphi}{\partial \cdot_i}g\right) - 0$$

$$\frac{\partial\varphi}{\partial a} + \sum_i \left(\frac{\partial\varphi}{\partial c_i}\overline{c'_i} + \frac{\partial\varphi}{\partial t_i}\overline{t'_i}\right) - \frac{\overline{d\varphi}}{da} = 0$$

but this is no other than equation (4), i.e. the equation which expresses the definition of adiabatic invariants.

In this manner the problem set in the introduction: to derive a general method of finding adiabatic invariants, has been solved. Before discussing the more general applications two special problems — classical ones for the quantumhypothesis — may be treated by our method.

5 (A). *The linear oscillator*. The parameter is here the frequency. The solution is as follows:

$$H = \tfrac{1}{2}p^2 + \tfrac{1}{2}a^2q^2 = c_1, \quad p = F = \sqrt{2c_1 - a^2q^2} \quad V = \int dq\, F = \int dq \sqrt{2c_1 - a^2q^2} \quad (13)$$

$$\frac{\partial V}{\partial a} = -\int dq\, \frac{aq^2}{F} \qquad \frac{\partial V}{\partial c_1} = \int \frac{dq}{F} = t_1 \quad \ldots \quad (14)$$

$$c'_1 = \frac{\partial}{\partial t_1}\left(\frac{\partial V}{\partial a}\right) = \frac{\partial}{\partial q}\left(\frac{\partial V}{\partial a}\right) \cdot \frac{dq}{dt_1} = aq^2 = \frac{1}{a}a^2q^2 \quad \ldots \quad (15)$$

The mean value of the right-hand side is c_1/a. Thus we obtain the well-known adiabatic invariant c_1/a.

B. *Body rotating about a fixed axis*. Calling the moment of inertia (the parameter) A and the moment of momentum p, we have:

$$H = \frac{1}{2A}p^2 = c_1 \quad p = F = \sqrt{2\,Ac_1} \quad V = \int dq\, F = q\,\sqrt{2Ac_1} \quad \ldots \quad (16)$$

$$\frac{\partial V}{\partial A} = \frac{c_1 q}{F} \qquad \frac{\partial V}{\partial c_1} = \frac{Aq}{F} = t_1 \qquad \left(\frac{\partial V}{\partial A}\right) = \frac{c_1}{A}t_1 \quad \ldots \quad (17)$$

$$c'_1 = -\frac{\partial}{\partial_1}\left(\frac{\partial V}{\partial A}\right) = -\frac{c_1}{A} \quad \ldots \ldots \ldots \quad (18)$$

which gives $c_1 A = $ const., hence also $p = T = \sqrt{2Ac_1} = $ const.

APPLICATIONS.

6. *The cyclic system*. We call *cyclic* those co-ordinates which do not occur in the expression for the Hamiltonian function (ignorable co-ordinates according to THOMSON and TAIT's terminology). They will be indicated by q_x $(x = 1, 2, \ldots, k)$, the remaining, non-cyclic co-ordinates by $q_\lambda^{\cdot}$ $(\lambda = k + 1,\ k + 2, \ldots, n)$.

Hence we have

$$H = H(q_\lambda, q_x, p_\lambda; a) \qquad \dot{p}_x = -\frac{\partial H}{\partial q_x} = 0 \qquad p_x = c_x \quad \ldots \quad (19)$$

The characteristic function now will be

$$V = \sum_x c_x\, q_x + W(q_\lambda, c_x, c_\lambda; a) \quad \ldots \ldots \ldots \quad (20)$$

We shall further assume that c_n is the energy-constant; we then obtain

$$\frac{\partial V}{\partial c_x} = q_x + \frac{\partial W}{\partial c_x} = t_x \qquad \frac{\partial V}{\partial c_\lambda} = \frac{\partial W}{\partial c_\lambda} = t_\lambda \quad \ldots \quad (20')$$

where all t, excepting t_n, are constants and $t_n = t + $ const.

From the equations for t_λ the q_λ may be derived as functions of the c_x, c_λ and t_λ. Further we have

$$\frac{\partial V}{\partial a} = \frac{\partial W}{\partial a} \qquad \ldots \ldots \ldots \ldots \quad (21)$$

from which it follows, that $\dfrac{\partial V}{\partial a}$ is a function of the c_x, c_λ and t_ℓ and independent of the t_x, hence:

$$c'_x = -\frac{\partial}{\partial t_x}\left(\frac{\partial V}{\partial a}\right) = 0 \qquad c_x = \text{adiab. Invar} \quad . \quad . \quad (22)$$

In the case, when $K = n$, i. e. when all the co-ordinates are cyclic, we have

$$H = H(p_i) \qquad p_i = c_i \qquad V = \sum_i c_i q_i \qquad (i = 1, 2, \ldots n) \ . \quad (23)$$

If the energy-constant c is a function of the c_i which is found by substituting the c_i in H, the new Hamiltonian function will be

$$K = C + \left(\frac{\partial V}{\partial a}\right)$$

But $\dfrac{\partial V}{\partial a}$ is equal to zero, hence all c_i are adiabatic invariants. As the co-ordinates corresponding to the moments c_i the old co-ordinates q_i must be taken — they are all linear functions of the time. This fact brings out the natural character of the method, hence it appears to be a very natural generalization of the method of reasoning followed in the theory of cyclic systems.

The simplest instance of a cyclic system — a body rotating about a fixed axis — was discussed above under 5.

7. *The conditionally periodic system.* As is well-known a condition-ally periodic system possesses besides the energy-integral $(n-1)$ other integrals which are of the second degree with respect to the moments. They all contain the moments only as squares, not as products, thus only p_i^2 and no $p_i p_x$. Solving the p_i^2 we get

$$p_i^2 = \psi_i(q_i, c_1 \ldots c_n) \qquad p_i = \sqrt{\psi_i} \quad (c_1 \ldots c_n \text{ integration const.}) \quad (24)$$

therefore each p_i depends only on the corresponding co-ordinates q_i. If the initial value of q_i lies in between two simple successive roots a_i and b_i of the equation $\psi_i = 0$, the co-ordinate displays librational motion. We shall here consider the case in which this holds for all the co-ordinates q_i.

The characteristic function V is now given by

$$V = \sum_i \int dq_i \, V \, \overline{\psi_i} \quad \ldots \quad \ldots \quad (25)$$

hence

$$\frac{\partial V}{\partial a} = \sum_i \int dq_i \, \partial V \, \overline{\psi_i}, \quad \frac{\partial V}{\partial c_x} = \sum_i \int dq_i \, \frac{\partial V \, \overline{4_i}}{\partial c_x} = t_x \quad . \quad (26, 27)$$

The first group of the rheo-parametric differential equations has the following form

$$\dot{c}_x = - \frac{\partial}{\partial t_x} \left(\frac{\partial V}{\partial a} \, \dot{a} \right)$$

or putting $a = const$ and substituting for $\partial V / \partial a$ its value from (26)

$$c'_x = - \frac{\partial}{\partial \dot{}_x} \left(\sum_i \int dq_i \, \frac{\partial V \, \overline{\psi_i}}{\partial a} \right) \quad . \quad . \quad . \quad . \quad (28)$$

Now it follows from (27) that the integral within the brackets depends on t_x only through the intermediary of the q_i (on c_x it depends explicitly and also through the q_i; hence

$$c'_x = - \left(\sum_i \frac{\partial V \, \overline{\psi_i}}{\partial a} \frac{\partial q_i}{\partial \dot{}_x} \right) \quad . \quad . \quad . \quad . \quad (28')$$

We have now on the left to put the line indicating the mean value and on the right actually to calculate the time-average. For this we need the following propositions: the curve of the orbit fills the whole region $a_i \leq q_i \leq b_i$ ($t = 1, 2 \ldots n$), the filling being everywhere "dense" [1]. The time-mean of an arbitrary function f of the phase of motion of the system, taken over an interval of time τ increasing indefinitely, may be replaced by the space-mean of the function over this region [2]. In the variable quantities c_i, t_i in order to compute the space-mean we have to integrate the function f over a "period-cell" and divide by the "volume" of the cell

$$\Omega = |\omega_{ix}| \quad \left(\omega_{ix} = \int dq_i \, \frac{\partial V \, \overline{\psi_i}}{\partial c_{\lambda}} = 2 \int_{a_i}^{b_i} dq_i \, \frac{\partial V \, \overline{\psi_i}}{\partial c_x} \right) . \quad . \quad (29)$$

hence:

$$\overline{f} = \lim \frac{1}{\tau} \int_{\tau} dt \, f = \frac{1}{\Omega} \int \overset{\cdots}{\Omega} \int dt_1 \ldots dt_n \, f \quad . \quad . \quad (30)$$

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[1] P. Stäckel. Math. Ann. 54 (1901) p. 86. In the proof it is assumed that between the ω_{ix} (equation 29) no relations of commensurability exist.

[2] Comp. J. M. Burgers l. c. p. 200.

Representing by Ω_x the sub-determinants corresponding to the ω_{ix} the mean value of the right-hand side of (28′) after some reduction may be written in the form

$$-\frac{1}{\Omega}\sum_i \Omega_{ix}\, 2\int_{a_i}^{b_i}\frac{\partial\sqrt{\overline{\psi_i}}}{\partial a}\,dq_i \quad . \quad . \quad . \quad . \quad . \quad (31)$$

or putting

$$v_i = 2\int_{a_i}^{b_i} dq_i\,\sqrt{\overline{\psi_i}} \,. \quad . \quad . \quad . \quad . \quad . \quad (32)$$

and noticing that the integrand disappears at the limits of the integral, also in this form

$$-\frac{1}{\Omega}\sum_i \Omega_{ix}\frac{\partial v_i}{\partial a} \quad . \quad . \quad . \quad . \quad . \quad (31')$$

Hence we obtain the relation

$$\overline{c'_x}+\frac{1}{\Omega}\sum_i \Omega_{ix}\frac{\partial v_i}{\partial a}=0 \quad . \quad . \quad . \quad . \quad . \quad (33)$$

We now solve this set of equations for the derivatives $\partial v_i/\partial a$

$$\frac{\partial v_i}{\partial a}+\sum_x \omega_{ix}\,\overline{c'_x}=0 \quad . \quad . \quad . \quad . \quad . \quad (34)$$

Instead of ω_{ix} we may write

$$\omega_{ix}=\frac{\partial}{\partial c_x}\,2\int_{a_i}^{b_i} dq_i\,\sqrt{\overline{\psi_i}}=\frac{\partial v_i}{\partial c_x} \quad . \quad . \quad . \quad . \quad (35)$$

Hence instead of (34)

$$\frac{\partial v_i}{\partial a}+\sum_x \frac{\partial v_i}{\partial c_x}\overline{c'_x}=0 \quad . \quad . \quad . \quad . \quad . \quad (36)$$

The v_i are functions of a and of the c_x; the left-hand side of (36) therefore is the complete "adiabatic" derivative $\dfrac{dv_i}{da}$: hence the v_i are adiabatic invariants.

The above invariants have been obtained by submitting to the series of operations prescribed by our method the first group of our rheo-parametic equations, those for c'_x. We shall now show, that we need not proceed and that we need not consider the second group of equations, those for t'_x, at all, supposing our object to be to find the condition mentioned in the introduction under (2) which every quantum-quantity of the conditionally periodic system has to

satisfy. We may briefly formulate the condition mentioned under (1) by saying, that each quantum-quantity v must retain a constant value along the "orbit" of our system; it is a function of those integrals of the iso-parametric system which do not contain the time t explicitly, i.e. of $c_1, \ldots c_n, t_2, \ldots t_n$. The time-mean of v is therefore v itself. We may then replace this time-mean by the space-mean for the cell Ω; this being a function of the c_x and a, v is a function of the c_x and independent of $t_2, \ldots t_n$. Now we have found n adiabatic invariants, functions of c and a; the remaining ones, which have not been computed, all contain the t_x, hence we do not need these for our present purpose. The conditions (1) and (2) for a conditionally periodic system without commensurate relations between the w_{ix} therefore assume the form

$$\left.\begin{array}{l} v = funct\,(c_1, \ldots c_n \,;\, a) \\[2mm] v = funct\,(v_1, \ldots v_n) \end{array}\right\} \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (37)$$

where the v_x are given by equation (32). We know, that the quantum-theory chooses as quantum-quantities the v_x themselves [1]).

§ 8. *The ergodic system.* So far we have assumed that the iso-parametric problem is actually solved. Now we shall only suppose, that the energy-integral

$$H\,(p_i, q_i, a) = c_1 \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (38)$$

is given and in addition introduce the "ergodic" hypothesis that the system passes through every point of the "energy-surface" $H = c_2$ [2]). The time-mean F of a phase-function f is then given by

$$\bar{f} = \left.\frac{\displaystyle\int \ldots \int dp_2 \ldots dp_n\, dq_1 \ldots dq_n \frac{1}{\dot{q}_1} f}{\displaystyle\int \ldots \int dp_2 \ldots dp_2\, dq_1 \ldots dq_n \frac{1}{\dot{q}_1}}, [3])\right\} \quad \cdot \quad \cdot \quad \cdot \quad (39)$$

the integrals being taken over the energy-surface $H = c_t$.

As a very natural specialisation of our general method we now take as transformation-function V the quantity

$$V = \int F dq_1 \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (40)$$

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[1]) K. SCHWARZSCHILD. Sitzungsber. Berlin 1916. p. 550. P. EPSTEIN. Ann. d. Phys. 50 (1916) p. 489; 51 (1916) p. 168. A. SOMMERFELD. Ann. d. Phys. 51 (1916) p. 1.

[2]) Cf P. and T. EHRENFEST. Enc. d. math. Wiss. IV 32. § 10.

[3]) L. BOLTZMANN. Gastheorie II p. 88. and seq.

F being the expression for p_1 which is obtained by solving $H = c_1$

$$p_1 = F(p_2 \ldots, p_n, q_1, \ldots, q_n, c_1; a) \quad \ldots \quad \ldots \quad (41)$$

When this expression is substituted in $H = c_1$ the result will be an identity. By differentiating this with respect to $c_1, p_2, \ldots, p_n, q_1, \ldots, q_n$, we find

$$\frac{\partial H}{\partial F} = \frac{1}{\frac{\partial F}{\partial c_1}}, \quad \frac{\partial H}{\partial q_i} = -\frac{\frac{\partial F}{\partial q_i}}{\frac{\partial F}{\partial c_1}}, \quad \frac{\partial H}{\partial p_x} = -\frac{\frac{\partial F}{\partial p_x}}{\frac{\partial F}{\partial c_1}} \Bigg\} \quad \ldots \quad \ldots \quad (42)$$

from which the Hamiltonian equations are easily derived as follows

$$\frac{\partial p_x}{\partial p_1} = \frac{\partial F}{\partial q_x} \qquad \frac{\partial q_x}{\partial q_1} = -\frac{\partial F}{\partial p_x} \qquad \frac{dt}{dq_1} = \frac{\partial F}{\partial c_1} \quad \ldots \quad (42')$$

Let us now form the derivatives of the transformation-function V with respect to all the variables which it contains:

$$\frac{\partial V}{\partial q_1} = F \quad \frac{\partial V}{\partial q_x} = \int \frac{\partial F}{\partial q_x} dq_1 = p_x \quad \frac{\partial V}{\partial p_x} = \int \frac{\partial F}{\partial p_x} dq_1 = q_x \quad \frac{\partial V}{\partial c_1} = \int \frac{\partial F}{\partial c_1} dq_1 = t_1 \quad (43)$$

Evidently V forms the transition from the variables $p_1, \ldots, p_n$, $q_1, \ldots, q_n$ to the variables $p_2, \ldots, p_n, q_2, \ldots, q_n, c_1, t_1$. Of all the rheoparametric differential equations we only need the equation for c' here, viz.

$$c'_1 = -\frac{\partial}{\partial t_1}\left(\frac{\partial V}{\partial a}\right) = -\frac{\partial}{\partial t_1}\left(\int \frac{\partial F}{\partial a} dq_1\right) \quad \ldots \quad \ldots \quad (44)$$

The integral inside the brackets only depends on t through q_1, hence

$$c'_1 = -\left(\frac{\partial F}{\partial a} \dot{q}_1\right) \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (44')$$

We now form the mean value according to (39):

$$\overline{c'_1} = \frac{-\int \ldots \int dp_2 \ldots dp_n \, dq_1 \ldots dq_n \dfrac{\partial F}{\partial a}}{\int \ldots \int dp_2 \ldots dp_n \, dq_1 \ldots dq_n \dfrac{\partial F}{\partial c_1}} \Bigg\} \quad \ldots \quad \ldots \quad (45)$$

where in the denominator $1/\dot{q}_1$ has been replaced by $\dfrac{\partial F}{\partial c_1}$ according to the last equation of the set $(42')$. It is easily seen, that the numerator and denominator are the partial derivatives with respect to a and c, respectively of a function V of the form

$$V = \int \ldots \int dp_1 \ldots dp_n \, dq_1 \ldots dq_n, \quad \ldots \quad \ldots \quad (46)$$

the integration extending over the region enclosed by the energy-surface $H = c_1$. We thus have

$$\frac{\partial V}{\partial a} + \frac{\partial V}{\partial c_1} \overline{c'_1} = 0 \quad \ldots \ldots \ldots \quad (47)$$

hence V is an adiabatic invariant. It can also easily be shown that this quantity has a meaning which is independent of the system of co-ordinates used; it therefore also satisfies the condition mentioned in the introduction under (3). The same is true for the quantity called v in § 3, b.

It remains to be seen under what conditions the quantities v_1 defined by equation (32) also satisfy this requirement. It may be expected that this enquiry will teach us how to quanticize systems which are "degenerated" in different ways. It also seems very probable, that this question will be decided on the lines indicated by PLANCK [1]) and SCHWARZSCHILD [2]). For instance, as regards the movement of a top on which no external forces are acting, of the three adiabatic invariants: the moment of momentum, its projection on the axes of the figure and its projection on ζ-axes of a fixed system of coordinates of arbitrary orientation (all three multiplied by 2π) only the first two may be quanticized. The "elementary region" thus will be not h^3 but $h^3 (2n_1 + 1)$, where n_1 is the quantum-number corresponding to the moment of momentum. On this ground exception may be taken to EPSTEIN's calculation of the specific heat of hydrogen [3]). To all these problems — problems relating to the adaptation of the quantum-hypothesis to different cases — I hope to return soon.

The method above developed is independent of this question, it is the solution of a purely mechanical problem. It seems advisable to try and apply it to systems which cannot be integrated by a separation of the variables in HAMILTON-JACOBI's partial differential equation, e.g. to the POINSOT-motion. About this question also I hope to be able to make a communication shortly.

Petrograd, September 1918.   *Physical Laboratory of*
                                                  the University.

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[1]) M. PLANCK. l. c.

[2]) K. SCHWARZSCHILD. Sitzungsber. Berlin 1916. p. 550.

[3]) P. S. EPSTEIN. Ber. d. D. Phys. Ges. 1916 p. 398. Compare especially (10) on p. 401. Objections may also be made to the quanticizing proposed on p. 407, seeing that the quantum-quantities in that case are not adiabatic invariants,

PROCEEDINGS

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CONTENTS.

Chemistry. — "*Urease and the radiation-theory of enzyme-action*".
By Dr. H. P. BARENDRECHT.

(Communicated in the meeting of February 22, 1919).

I.

1. Since the discovery by TAKEUCHI of urease in the Soja-beans an exceptionally useful material for the study of enzyme-action has been at our disposal. The enzyme as well as the pure substrate, urea, are now readily obtainable in unlimited quantity. The estimation of the reaction products can be carried out easily and accurately, an important condition for success in pioneerswork, where innumerable analyses have to be made.

This chance of solving to some extent the great riddle of enzyme-action has therefore attracted many workers during the last few years.

MARSHALL (J. Biol. Chem. XVII, p. 351, 1914) has found, that in this case also the action is proportional to the concentration of the enzyme.

The ARMSTRONG's, HORTON and BENJAMIN (Proc. Roy. Soc. 1912 and 1913) have made extensive empirical studies, from which they drew the conclusion, that ammonia retards, but carbonic acid accelerates the reaction, a surprising result, which others also state to have found. As will be seen from the present paper, pure chemical empiricism here leads to false conclusions.

A first endeavour to theoretical as well as to experimental study of the action of urease was made by DONALD VAN SLYKE and his collaborators (J. Biol. Chem. XIX, p. 141, 1914).

To clear the field it is necessary to pass some criticism on this work.

The theory of these authors and all their further work are based principally on three experiments. In experiments 1 and 2 "the effect of concentration of urea, enzyme concentration being constant" and "the effect of decreasing urea concentration on reaction, as the latter approaches completion" were investigated. As in these experiments the considerable changes in concentration of the hydrogen-ions were left out of consideration, notwithstanding the authors themselves have further on become aware, that the urease activity is dependent in a high degree on the H-ion concentration, it is no wonder, that they

tried to found the "formulation of the nature and course of the reaction" especially on experiment 3, in which phosphates acted as a buffer against large changes of the true acidity.

Since the results, as published, of this experiment, were incompatible with the experiments and theory of the present papers, the author has recalculated them on the basis of VAN SLIJKE's own theory.

The remarkable conclusion is, that even VAN SLIJKE's own basal experiment was not at all in accordance with his own theory, the c being clearly far from constant:

TABLE III of VAN SLIJKE.
$$E = 0,1 \qquad t = 60.$$

Concentration urea.	a. 0,01 N NH_3 calc. for complete decomp. of urea.	x. 0,01 N NH_3 formed.	$0,4343\ c = \dfrac{d}{dEt-x} \log \dfrac{a}{a-x}$ acc. to v. SLIJKE.	$0.4343\ c$ $\dfrac{d}{dEt-x} \log \dfrac{a}{a-x}$ recalculated
per cent	c.c.			
0.0375	12.5	5.8	0.055	0.056
0.075	25.—	10.4	0.058	0.059
0.15	50.—	15.5	0.053	0.054
0.3	100.—	21.2	0.052	0.054
0.6	200.—	24.8	0.051	0.048
1.2	400.—	27.—	0.052	0.039
2.4	800.—	28.5	0.052	0.032

2. *The general equation of urease action.*

The investigations, published in this paper, were again based on the author's hypothesis, that an enzyme acts by radiation and that an enzyme particle contains the same molecule, which is liberated or acted upon by this enzyme, in some active state. In his first papers on enzyme action (Proc. K. Akad. Wetensch. Amsterdam 1904; Zeitschr. physikal. Chem. XL, p. 456, 1904; Biochem. J. VII, p. 559, 1913) the author has already suggested, that the radiation, by which enzymes exert their action, is due to the electrons, forming part of the atoms. The recent development of the electron theory of matter has revealed, that, every atom being a complex of positive and negative electrical units, all chemical action is in reality an electric phenomenon. In a general way it may be stated, that in an atom the electrons, moving round the positive nucleus, will have some effect e.g. of electromagnetic induction on other atoms in their neighbourhood.

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If all the atoms, constituting a molecule, receive this radiation from a similar molecule at the same time in the required phase, the reactivity of the molecule as a whole can be expected to have changed. A small increase of the vibration of the molecule may increase its power to enter into combination (this point will be treated further on), a large elevation may tear it out of a compound with other molecules.

However, the author wishes not at present to lay much stress on the particulars of his hypothesis. The numerous experimental facts, recorded in these papers, for a great deal only revealed by the aid of this guiding hypothesis and which we have all coordinated by drawing their consequences, will prove its usefulness.

The radiation, by means of which urease acts on urea, thus originates from the enzyme molecule and is able to exert its hydrolysing effect to a certain distance, probably microscopically small.

When this urease-radiation strikes a urea-molecule, it is absorbed, just as for instance the specific radiation of a Na-atom is especially absorbed by a Na-atom.

The amount of urea, hydrolysed in a time-unit by an enzyme-molecule would therefore be independent of the urea-concentration, if the other constituents of the solution had practically no absorbing power towards this radiation. Only with a very small concentration of urea, the radiation might be expected to be, at least partially, so much weakened by spreading before striking a urea-molecule, that it has lost the power of hydrolysing it. Hence for very dilute solutions of urea constancy of action of a given quantity of urease should not be expected; in these conditions the amount of action will be found smaller.

So far the theory is the same as that, put forward by the author previously for the sugar-enzymes.

A new point of dominating importance, at least in the case of urease, is, that the hydrogen-ions proved to be, besides urea, the only constituent in the solution, which absorbs this radiation.

It seems not improbable, that the way in which the H-ions were found to interfere with the urease-action will appear to play a part also in enzyme-action generally.

The mathematical formulation of this theory is very simple and gives at once the following differential equation for the reaction velocity at constant temperature and constant H-ion concentration:

$$- dx = m \frac{x}{x + nc} dt \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In this equation x is the concentration of the urea (grams per

100 c.c.), c is the concentration of the H-ions (also in grams per 100 c.c.) and n is the coefficient of absorption of the H-ions, i.e., one gram of H-ions absorbs n times as much radiation as one gram of urea.

The velocity-constant m for a given temperature and H-ion concentration is proportional to the concentration of enzyme only, if both temperature and H-ion concentration are maintained really constant.

Calling the initial urea concentration a, expressed like x and c in grams per 100 c.c., putting

$$\frac{a-x}{a} = y,$$

substituting this in (1), we get

$$a\,dy = m\,\frac{a\,(1-y)}{a\,(1-y)+nc}\,dt \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

After integration and introduction of decimal logarithms the general equation for the reaction-velocity of urease at constant temperature and constant H-ion concentration becomes

$$\frac{nc}{0,434}\,log\,\frac{1}{1-y} + ay = mt \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

3. *Determination of the constant n.*

For the estimation of the important constant n it was necessary, not only to determine accurately the H-ion concentration c, but also to take care, that c and thereby also m (as will be seen further on) remained unchanged from beginning to end of the reaction. Now, the hydrolysis of urea to ammonium-carbonate is in so far a difficult case for enzyme study, that here by the enzyme-action itself a distinctly alkaline substance is formed out of a neutral substrate. This production of alkali is so considerable, that even in presence of a buffer mixture of 8 °/₀ phosphate only 0.01 °/₀ or at the utmost 0.02 °/₀ of urea can be allowed to be transformed, if one wants to maintain anything like constancy of p_H.

A study of the kinetics of urease-action without the addition of a powerful buffer to keep the true reaction constant, is evidently as useless as working without a thermostat in a room of widely changing temperature.

In fixing the best conditions for the experimental determination of this constant n, two considerations determined the choice of the p_H of the regulating phosphate mixture.

As m had appeared to be a function of p_H with a distinct maximum, the p_H of this maximum would offer the advantage, that here a small variation of p_H would produce smaller change in m than elsewhere.

Secondly, to check the influence of the inavoidable experimental errors, the coëfficient $\dfrac{nc}{0,434}$ should not be much larger or smaller than a. For, if the coëfficient of $log \dfrac{1}{1-y}$ predominates largely, the reaction practically corresponds to the ordinary logarithmic line of the law of mass action. On the other hand, a being much larger, a nearly straight line will appear.

Therefore in these basal experiments a mixture of Na_2HPO_4 2 aq and KH_2PO_4 was used in such proportion, that the enzyme-action would proceed in an 8 % phosphate mixture of about $p_H = 7.5$.

The materials used were the following:

Ordinary yellow (probably Mantchourian) Soja-beans were powdered in a small American "Enterprise" mill, slowly turning the handle to avoid the heating by friction, which is otherwise soon perceptible. The powder was kept in a common stoppered bottle in the dark.

The KH_2PO_4 and Na_2HPO_4 2 aq were the purest compounds from KAHLBAUM, labelled "zu Enzym-studien nach Sörensen".

The urea, from KAHLBAUM, was recrystallised by the author from alcohol of 96 %.

All experiments in this research were made at a temperature of 27° C. This temperature is just high enough to allow without difficulty the use of a waterbath of constant temperature nearly the whole year round, and, on the other hand, low enough to avoid the deteriorating effect of higher temperatures on enzyme activity, within reasonable limits of time and true reaction.

7.28 g. of Na_2HPO_4 2 aq and 2.32 g. of KH_2PO_4 were dissolved in a stoppered flask to 100 c.c.

Into this solution 0.4 gram of Soja-meal was introduced, the flask was shaken thoroughly and left in the waterbath of 27° for one hour. After addition of 0.4 gram of kiezelgur, which had been repeatedly washed and then dried, the extract was filtered off easily and perfectly clear through an ordinary pleated filter. In the mean time there had been prepared a solution of 14.4 grams of Na_2HPO_4 2 aq in 150 c.c. of water in a larger stoppered flask. To this were now added 75 c.c. of the clear Soja extract, by which a diluted, still perfectly clear, extract resulted, which will be indicated by the letter E.

Ten test-tubes of Jena-glass, about 20 cm. long and 2.3 cm. wide, had before been placed in the bath. These test-tubes were (as in VAN SLYKE's experiments) closed by rubber stoppers with two borings. Through one of these a glass tube passed, about 30 cm. long and 4 or 5 m.m. outside diameter, ending near the bottom in a little bulb with pinholes. The second boring held a small pipette-like tube, with some cottonwool in the narrow end at the top, which was meant to prevent the passage of any splashes of the liquid with the air-current.

Each of these test-tubes received 10 c.c. of the extract E. Together with the tubes a flask with 0.150 gram of urea, dissolved in 250 c.c. water, was placed in the thermostat.

After equilibrium of temperature had been established, 2 c.c. of urea solution were introduced in each test-tube with an accurate pipette. Like all the pipettes used in these experiments, this one was calibrated for blowing out one minute after the liquid had run out, which gives the greatest accuracy, provided of course, the inside is cleaned beforehand with a mixture of sulphuric acid and bichromate. A moment's stirring through the long tube with air, freed from carbon dioxide, ensured complete mixing. Both tubes were closed by pieces of rubber tubing and clips.

The moment the 2 c.c. had run out of the pipette and the contents of the test-tube had been provisionally mixed by shaking, was taken as the starting-point of the enzyme-action. As the 2 c.c. ran out of the pipette in a few seconds this point could be determined with sufficient accuracy.

In a wooden block with two rows of holes (see Figure 1) the necessary number of thickwalled glass tubes were kept ready, each containing a carefully measured quantity, between 5 and 12 cc., of sulphuric acid $\frac{1}{50} N$, and filled up with water to a height of about 7 cm. These tubes were also closed by a rubber stopper, through which passed a long tube with pinholes and a short one.

At the end of the fixed time-interval (or rather about $\frac{3}{4}$ minutes before it, as this was within a few seconds, the time required for the next operation till the reaction was considered to have stopped) the test-tube was taken out of the thermostat and put into the wooden block. The rubber tubing B being connected with the glass tube, the clip was removed, the closing of the tube A was taken off and replaced by a piece of rubber tubing, in the open end of which was then put a drop of octylalcohol to prevent foaming. Immediately after this the point of a pipette with about 25 cc. of saturated potassium carbonate solution was introduced into this rubber tubing

and by blowing out its contents rapidly and then blowing through air for a moment, the potassium carbonate solution was mixed
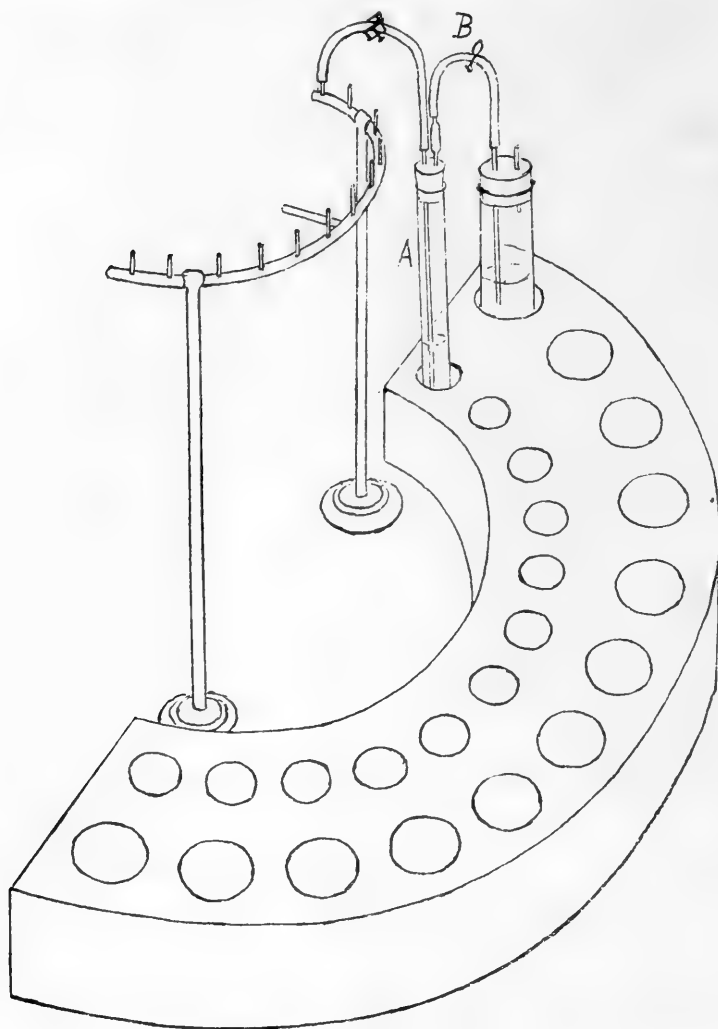
Fig. 1.

within a few seconds with the liquid in the reaction tube, stopping the enzyme-action abruptly.

The tube A was then connected with the air-supply and the ammonia blown over by a vigorous current of air, washed through sulphuric acid. Two hours was proved to be amply sufficient for the quantities of liquid used.

Larger volumes would have been difficult to handle.

In order to obtain sufficient accuracy in estimating these very small quantities of NH_3 single determinations were not sufficient. On two consecutive days identical series of experiments were carried

out in duplo, without changing the sulphuric acid tubes. In this way each absorbing tube got four times the amount of NH_3 of one test-tube. On each day the Soja extract was freshly prepared as described above.

The necessary correction for the traces of NH_3, which might have been given off by the Soja-meal, the phosphate or the potassium carbonate, was determined by placing each day 3 times 10 cc. of extract E into 3 empty test-tubes and after the addition of 25 cc. of potassium carbonate, blowing over the NH_3 in the same manner into absorbing tubes, filled with 5 cc. of H_2SO_4 $^1/_{50}$ N and water. Each of these absorbing tubes thus received 6 times the amount of this correction.

The estimation of p_H was made electrometrically in the air-thermostat of 27°, as described further on in this paper.

In the present case for 10 cc. extract E, mixed with 2 cc. water $p_H = 7.515$.

10 cc. of extract E, mixed with 2 cc. of urea solution (0.06 %) after 4 hours standing at 27° gave $p_H = 7.525$.

As the p_H on a total hydrolysis of 0.01% urea in 8% phosphate showed the slight increase of 0.01, it was taken here as 7.52.

The titration was carried out directly in the wide absorbing tube with $^1/_{50}$ N NaOH, prepared shortly before with distilled water, freed from carbon dioxide and $^1/_{10}$ N NaOH solution, prepared and and kept free from CO_2.

A very dilute solution of sodium alizarin sulphonate proved again to be the best indicator for NH_3 estimations. Cleaning of burettes and pipettes with bichromate and sulphuric acid directly before use is absolutely necessary in this kind of work.

Jan. 17—18 1917.   TABLE 1.   (Fig. 2 A)

0.01 % urea. $p_H = 7.52$

t minutes.	c.c. $\frac{1}{50}$N H_2SO_4	c.c. $\frac{1}{50}$N NaOH	c c. $\frac{1}{50}$N NH_3	c.c. $\frac{1}{50}$N NH_3 correct.	y	$m = \dfrac{0.0327 \, log \frac{1}{1-y} + 0.01y}{t}$
20	10	8.1	1.9	1.78	0.223	0.000290
30	10	7.3	2.7	2.58	0.323	0.000292
50	10	6.2	3.8	3.68	0.46	0.000267
70	10	4.8	5.2	5.08	0.635	0.000295
90	10	4.0	6.0	5.88	0.735	0.000291
110	12	5.37	6.63	6.51	0.814	0.000291

As will be also seen in Fig. 2 A the point for $t = 50$ falls outside
the curve and is evidently erroneous.
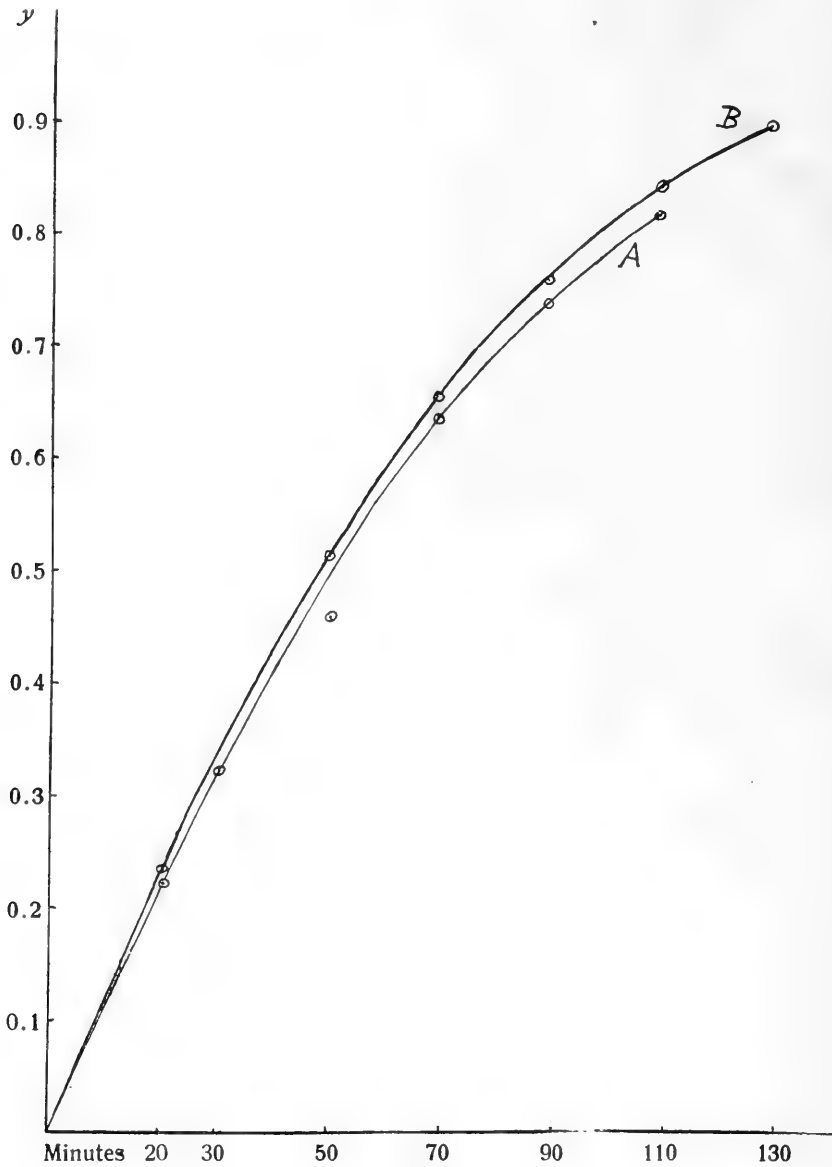
Fig. 2.

By combining the pairs of values, which are sufficiently wide
apart on this curve, the equation $m = \dfrac{1}{t} \left(\dfrac{nc}{0,434} \, log \, \dfrac{1}{1-y} + 0,01y \right)$
gives the following figures for $\dfrac{nc}{0,434}$. (Table 2).

The concentration of the hydrogen-ions in this equation had to

TABLE 2.

t	$\dfrac{nc}{0.434}$
20 and 90	0.0314
20 and 110	0.0318
30 and 90	0.0335
30 and 110	0.0334

mean 0.0327

be expressed in the same units as the concentration of the urea, in grams per 100 c.c. As $p_H = 7.52$ means a hydrogen-ion concentration of $10^{-8} \times 3{,}02$ in the usual units, grammolecules per Litre, we have here $10^{-8} \times 0{,}302$ g. H. in 100 c.c.

From this $n = 0{,}047 \times 10^8$.

In order to show, that in these estimations a high accuracy is wanted, but is hardly to be expected in the result, and that the deviations are within the limits of experimental errors, we may, for instance, calculate $\dfrac{nc}{0{,}434}$, assuming that for $t = 20$ the titration had given 8.05 instead of 8.1.

From

$$\frac{1}{20}\left(\frac{nc}{0{,}434}\,0{,}5768 + 0{,}00735\right) = \frac{1}{90}\left(\frac{nc}{0{,}434}\,0{,}1128 + 0{,}00229\right)$$

would then follow $\dfrac{nc}{0{,}434} = 0{,}0426$.

Considering, that the two small samples of Soja-meal, weighed

Jan. 31st 1917.   TABLE 3.   (Fig. 2 B)

t minutes.	c.c. $\frac{1}{50}$N H_2SO_4	c.c. $\frac{1}{50}$N NaOH	c.c. $\frac{1}{50}$N NH_3	c.c. $\frac{1}{50}$N NH_3 correct.	y	$m = \dfrac{0{,}0302\,log\,\frac{1}{1-y} + 0{,}01y}{t}$
20	5	4.03	0.97	0.94	0.235	0.000293
50	5	2.92	2.08	2.05	0.513	0.000291
70	5	2.35	2.65	2.62	0.655	0.000293
90	5	1.95	3.05	3.02	0.755	0.000289
110	5	1.62	3.38	3.35	0.838	0.000293
130	5	1.40	3.60	3.57	0.892	0.000293

off on two consecutive days might not have been absolutely equal, the author made a new set of experiments, in which only the two series of the same day were combined. (Table 3).

From this table was calculated:

TABLE 4.

t	$\dfrac{nc}{0.434}$
20 and 50	0.0343
20 and 110	0.0301
20 and 130	0.0302
50 and 110	0.0282
50 and 130	0.0287
70 and 110	0 0298
70 and 130	0.0300

mean 0.0302

The measurement for 90 minutes contains, as will be seen in the m-column of table 3 a comparatively large experimental error. Therefore the values, calculated with the aid of this estimation have been discarded from table 4.

Since of the many experiments of this kind that the author has carried out, this series was the most sucessful one, as to regularity, and in view of the smallness of the numbers, which had to be determined by titration, had given also a perfectly satisfactory result, the final value of $\dfrac{nc}{0,434}$ was taken to be 0,0302.

From this it follows, that
$$n = 0,043 \times 10^8$$
which value is used throughout in the course of this study and is confirmed indirectly by the important numerical relations, which will be developed with the aid of it in the following parts.

4. *Experimental verification of the general equation of urease-action.*

Activity of enzyme dependent on true reaction of the solution.

Experimental evidence will be brought forward in this part to show, that the formula

$$\frac{nc}{0,434} \log \frac{1}{1-y} + ay = mt$$

is really the general equation of urease-action at constant tempe-rature and constant H-ion concentration.

If $\dfrac{nc}{0,434}$ is small, compared to a, evidently the reaction curve must be expected to be practically a straight line. On the other hand the logarithmic curve of the simple law of mass action will appear to represent the course of the reaction in more acid solutions, where $\dfrac{nc}{0,434}$ predominates largely over a small value of a.

By changing the proportion of Na_2HPO_4 2 aq and KH_2PO_4 in the $8^0/_0$ phosphate mixtures a great range of constant H-ion concen-trations could be covered. To secure the constancy of p_H throughout the course of the reaction, it was necessary to work always with $0.02\ ^0/_0$, or better still with $0.01\ ^0/_0$ urea solutions. Since 12 c.c. of $0.01\ ^0/_0$ contain only 1.2 mg. of urea, this means, that in all these experiments the degree of hydrolysis of 1.2 mg. urea had to be determined by single measurements, a serious disadvantage, which, however, had to be put up with in view of the dominating impor-tance of constant H-ion concentration.

The same high degree of accuracy, as was absolutely necessary in the determination of the constant n, is not to be expected here, nor, happily, is it required.

A second object of these experiments was to determine m in the solutions of different acidity, when equal or comparable amounts of enzyme were present or in other words to investigate m as a function of p_H.

To get comparable amounts of enzyme in the solutions the following simple method proved to be efficient.

Some 500 grams of powdered Soja-beans were kept stored for this purpose in a stoppered bottle, shut off from the influence of light in a cupboard, and simply mixed now and then by shaking in the course of these experiments, which lasted several months.

The quantity of Soja-meal required was always weighed off and extracted on the day of the experiment with the same nearly neutral solution of 7.28 gr. of Na_2HPO_4 2 aq $+$ 2.32 gr. of KH_2PO_4 per 100 cc. of water. This extraction was performed by mixing Soja-meal and phosphate-solution in a stoppered flask, shaking through thoroughly, leaving it for one hour in the water-thermostat at 27°, adding kiezelgur of the same amount as the Soja-meal, and filtering rapidly through an ordinary pleated filter. Invariably, without any difficulty, a clear solution was obtained, slightly opalescent if large quantities of Soja-meal had been employed. The working solution

was then prepared by mixing this filtrate with the required volume of 9.6 °/₀ solution of Na_2HPO_3 2 aq and KH_2PO_4. A row of Jena test-tubes, each with 10 cc. of this liquid, was placed in the thermostat together with a 250 or 500 cc. flask with a 0.12 °/₀ or a 0.06 °/₀ urea solution, in short, the same methods were followed as described above in the determination of the constant n.

Some preliminary experiments had shown, that m, as calculated with our formula, was small at low and at high H-ion concentration, and that two hours' standing at 27° was already somewhat destructive to the enzyme in distinctly alkaline solution, not, however, in acid ones.

Unless the acidity has been too high, the diminution of the urease-activity by acids is a reversible process, like the neutralisation of a basic substance.

This fact was established by experiments, the particulars of which will be omitted here for want of space.

In Sept. 1916 the following series of experiments was made with 0.02 °/₀ urea. The correction for the traces of NH_3, developed from the materials employed, was estimated in the ordinary way by collecting these small quantities from 3 tubes, each with 10 cc. extract, in the same absorbing tube with 5 cc. H_2SO_4 ¹/₅₀ N.

In order to meet the possible objection, that the enzyme might have suffered by the influence of time, temperature and true reaction, in both the last experiments a tube with 10 c.c. of the same mixture as contained in the other ones, was left for 4 hours in the bath before introducing into it 2 c.c. of urea solution. After 60 minutes the same amount of urea was found to have been hydrolysed as recorded in tables 10 and 11. As mentioned before and as will be demonstrated more extensively further on, the stability of urease is still greater at lower p_H.

These experiments already confirm the theory. At high H-ion concentration the course of the reaction, as seen by comparison of the last columns, is practically identical with that which can be represented by the law of mass-action. The lower this concentration, the more it deviates from it and approaches to a straight line, just in the same degree, as predicted by the formula:

$$m = \frac{\dfrac{nc}{0,434} \, log \, \dfrac{1}{1-y} + ay}{t}.$$

By taking as the unit of urease concentration 1 gram of Soja to 150 cc. total 9.6 °/₀ phosphate solution and reducing to this the

TABLE 5.

3 gr. Soja in 100 c.c. $\begin{cases} 7.28 \text{ gr. } Na_2HPO_4 \text{ 2 aq.} \\ 2.32 \text{ gr. } KH_2PO_4 \end{cases}$

50 c.c. filtrate mixed with 100 c.c. water $+ \begin{cases} 1.92 \text{ gr. } Na_2HPO_4 \text{ 2 aq.} \\ 7.68 \text{ gr. } KH_2PO_4 \end{cases}$

$pH = 6.13$

t minutes.	c.c. NaOH $\frac{1}{50}$ N	c.c. NH$_3$ $\frac{1}{50}$ N corrected.	y	$m = \dfrac{0,74 \, log\frac{1}{1-y} + 0,02y}{t}$	$k = \dfrac{log\frac{1}{1-y}}{t}$
60	9.3	0.6	0.15	0.00090	0.00118
90	9.1	0.8	0.20	0.00082	0.00108
120	8.9	1.—	0.25	0.00079	0.00104
150	8.65	1.25	0.31	0.00082	0.00107
180	8.45	1.45	0.36	0.00082	0.00108
210	8.2	1.7	0.425	0.00087	0.00114
240	8.05	1.85	0.46	0.00084	0.00111
270	7.8	2.1	0.525	0.00090	0.00120
315	7.7	2.2	0.55	0.00083	0.00110
370	7.5	2.4	0.60	0.00081	0.00107

Mean 0.00084

$\frac{1}{3} \times 0.00084 = 0.00028.$

TABLE 6.

3 gr. Soja in 100 c.c. $\begin{cases} 7.28 \text{ gr. } Na_2HPO_4 \text{ 2 aq.} \\ 2.32 \text{ gr. } KH_2PO_4 \end{cases}$

50 c.c. filtrate mixed with 100 c.c. water $+ \begin{cases} 3.84 \text{ gr. } Na_2HPO_4 \text{ 2 aq.} \\ 5.76 \text{ gr. } KH_2PO_4 \end{cases}$

$pH = 6.40$

t minutes.	c.c. NaOH $\frac{1}{50}$ N	c.c. NH$_3$ $\frac{1}{50}$ N corrected.	y	$m = \dfrac{0,394 \, log\frac{1}{1-y} + 0,02y}{t}$	$k = \dfrac{log\frac{1}{1-y}}{t}$
30	9.3	0.6	0.15	0.00103	0.0023
60	8.8	1.1	0.275	0.00101	0.0023
90	8.4	1.5	0.375	0.00098	0.0023
125	7.95	1.95	0.488	0.00100	0.0023
150	7.6	2.3	0.575	0.00105	0.0025
180	7.4	2.5	0.625	0.00101	0.0024
215	7.1	2.8	0.70	0.00102	0.0024
240	6.95	2.95	0.738	0.00102	0.0024
270	6.75	3.15	0.788	0.00104	0.0025
300	6.6	3.3	0.825	0.00105	0.0025

Mean 0.00102

$\frac{1}{3} \times 0.00102 = 0.00034.$

TABLE 7.

0.75 gr. Soja in 100 c.c. $\begin{cases} 7.28 \text{ gr. } Na_2HPO_4 \text{ 2 aq.} \\ 2.32 \text{ gr. } KH_2PO_4 \end{cases}$

50 c.c. filtrate mixed with 100 c.c. water $+ \begin{cases} 8.64 \text{ gr. } Na_2HPO_4 \text{ 2 aq.} \\ 0.96 \text{ gr. } KH_2PO_4. \end{cases}$

$p_H = 7.21$

t minutes.	c.c. NaOH $\frac{1}{50}$ N	c.c. $NH_3 \frac{1}{50}$ N corrected.	y	$m = \dfrac{0{,}0611 \, log\frac{1}{1-y} + 0{,}02\,y}{t}$	$k = \dfrac{log\frac{1}{1-y}}{t}$
20	9.05	0.95	0.238	0.00060	0.0060
40	8.3	1.7	0.425	0.00058	0.0060
60	7.7	2.3	0.575	0.00057	0.0062
80	7.22	2.78	0.695	0.00057	0.0064
100	6.85	3.15	0.788	0.00057	0.0067
120	6.55	3.45	0.86	0.00058	0.0071
150	6.35	3.65	0.91	0.00055	0.0070
180	6.25	3.75	0.94	0.00052	0.0068
210	6.1	3.9	0.975	0.00056	0.0076

Mean 0.00057

$\frac{4}{3} \times 0.00057 = 0.00076.$

TABLE 8.

Two equal experiments, one on Sept. 18th, 1916, another with freshly prepared solution on Sept. 19th, 1916.

0.75 gr. Soja in 100 c.c. $\begin{cases} 7.28 \text{ gr. } Na\,HPO_4 \text{ 2 aq.} \\ 2.32 \text{ gr. } KH_2PO_4. \end{cases}$

50 c.c. filtrate mixed with 100 c.c. water $+$ 9.6 gr. Na_2HPO_4 2 aq.

$p_H = 7.52$

t minutes.	c.c. NaOH $\frac{1}{50}$N		c.c. $NH_3 \frac{1}{50}$ N corrected (mean).	y	$m = \dfrac{0{,}0302 \, log\frac{1}{1-y} + 0{,}02y}{t}$	$k = \dfrac{log\frac{1}{1-y}}{t}$
20	8.55	8.50	1.45	0.36	0.00065	0.0097
40	7.4	7.4	2.575	0.64	0.00065	0.0111
60	6.75	6.7	3.25	0.81	0.00063	0.0120
80	6.3	6.25	3.7	0.925	0.00066	0.0141
100	6.15	6.1	3.85	0.96	0.00061	0.0140

Mean 0.00064

$\frac{4}{3} \times 0.00064 = 0.00085$

TABLE 9.

0.5 gr. Soja in 100 c.c. $\left\{\begin{array}{l} 7.28 \text{ gr. Na}_2\text{HPO}_4 \text{ 2 aq.} \\ 2.32 \text{ gr. KH}_2\text{PO}_4 \end{array}\right.$

50 c.c. filtrate mixed with 150 c.c. water $+$ 14.4 gr. Na$_2$HPO$_4$ 2 aq.

$pH = 7.64$

t minutes.	c.c. NaOH $\frac{1}{50}$ N	c.c. NH$_3$ $\frac{1}{50}$ N corrected.	y	$m = \dfrac{0,0227 \log\frac{1}{1-y}+0,02y}{t}$	$k = \dfrac{\log\frac{1}{1-y}}{t}$
20$^1/_2$	9.2	0.8	0.20	0.00030	0.0048
40	8.4	1.6	0.40	0.00032	0.0055
60	7.72	2.28	0.57	0.00033	0.0061
80	7.3	2.7	0.675	0.00031	0.0061
100	6.8	3.2	0.80	0.00032	0.0070
120	6.5	3.5	0.875	0.00032	0.0075
150	6.2	3.8	0.95	0.00032	0.0087

Mean 0.00032

$2 \times \frac{4}{3} \times 0.00032 = 0.00085.$

TABLE 10.

0.5 gr. Soja in 100 c.c. $\left\{\begin{array}{l} 7.28 \text{ gr. Na}_2\text{HPO}_4 \text{ 2 aq.} \\ 2.32 \text{ gr. KH}_2\text{PO}_4 \end{array}\right.$

50 c.c. filtrate mixed with 200 c.c. water $+$ 19.2 gr. Na$_2$HPO$_4$ 2 aq.

$pH = 7.75$

t minutes.	c.c. NaOH $\frac{1}{50}$ N	c.c. NH$_3$ $\frac{1}{50}$ N corrected.	y	$m = \dfrac{0,0176 \log\frac{1}{1-y}+0,02y}{t}$	$k = \dfrac{\log\frac{1}{1-y}}{t}$
20	9.27	0.73	0.18	0.00026	0.0043
40	8.65	1.35	0.34	0.00025	0.0045
60	8.1	1.9	0.475	0.00024	0.0047
80	7.7	2.3	0.575	0.00023	0.0047
100	7.2	2.8	0.70	0.00025	0.0062
120	6.85	3.15	0.79	0.00023	0.0056
150	6.45	3.55	0.89	0.00023	0.0064
180	6.2	3.8	0.95	0.00023	0.0072
210	6.1	3.9	0.975	0.00023	0.0076

Mean 0.00024

$2 \times \frac{5}{3} \times 0,00024 = 0,00080.$

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TABLE 11.

Repetition of the experiment of Sept. 25th.

$$pH = 7.75$$

t minutes.	c.c. NaOH $\frac{1}{50}$N	c.c. NH$_3$ $\frac{1}{50}$ N corrected.	y	$m = \dfrac{0{,}0176\, log\frac{1}{1-y} + 0{,}02y}{t}$	$k = \dfrac{log\frac{1}{1-y}}{t}$
20	9.3	0.7	0.175	0.00025	0.0042
40	8.57	1.43	0.358	0.00026	0.0048
60	8.12	1.88	0.47	0.00024	0.0046
80	7.65	2.35	0.588	0.00022	0.0048
100	7.2	2.80	0.70	0.00025	0.0062
120	6.9	3.1	0.775	0.00022	0.0054
150	6.4	3.6	0.90	0.00024	0.0066
180	6.15	3.85	0.963	0.00025	0.0079
216	6.05	3.95	0.988	0.00025	0.0089

Mean 0.00024

calculated mean of m (as done at the foot of each table), we get
for equal enzyme concentration at different p_H the following list:

pH	Activity of the same quantity of urease
6.13	0.00028
6.40	0.00034
7.21	0.00076
7.52	0.00085
7.64	0.00085
7.75	0.00080

Mathematics. — *"Ueber topologische Involutionen."* By Prof. L. E. J. Brouwer.

Unter einer *topologischen Involution n-ter Ordnung* einer h-dimensionalen Mannigfaltigkeit F verstehen wir eine solche Zerlegung von F in Systeme von *höchstens* n Punkten, dass die Menge dieser Systeme sich eineindeutig und stetig auf eine als *Modulmannigfaltigkeit der Involution* zu bezeichnende h-dimensionale Mannigfaltigkeit M abbilden lässt.

§ 1. *Involutionen von Linien.*

Sei P ein Punkt der Modullinie M, der ein solches Segment s von M begrenzt, von dem jeder Punkt n verschiedene Bildpunkte auf der Linie F besitzt, während für P selbst $m > 1$ dieser Bildpunkte in einem Punkte Q von F zusammenfallen. Wenn wir einen Punkt C von s in hinreichender Nähe von P wählen, so zerfallen die weder P noch C entsprechenden, in der Nähe von Q gelegenen Punkte von F in drei und nur drei Kategorien: ein solcher Punkt ist nämlich *entweder* Bildpunkt eines zwischen C und P liegenden Punktes von M und lässt sich alsdann ohne Berührung der in der Nähe von Q liegenden Bildpunkte $D_1, D_2, \ldots D_m$ von C mit Q verbinden, *oder* Bildpunkt eines durch C von P getrennten Punktes von M, in welchem Falle er sich ohne Berührung von $Q, D_1, D_2, \ldots D_m$ aus der Nähe von Q entfernen lässt, *oder* schliesslich Bildpunkt eines durch P von C getrennten Punktes von M, in welchem Falle er sich sowohl ohne Berührung von $D_1, D_2, \ldots D_m$ mit Q verbinden, wie ohne Berührung von $Q, D_1, D_2, \ldots D_m$ aus der Nähe von Q entfernen lässt. Hiermit sind wir aber für $m > 1$ zu einem Widerspruch gelangt, so dass *jeder Punkt von M notwendig n verschiedene Bildpunkte auf F besitzt.* Hieraus folgt unmittelbar, *erstens*, dass F eine *geschlossene* Linie ist, *zweitens*, dass *die Involution n-ter Ordnung von F einer n-periodischen Rotationsgruppe topologisch äquivalent ist.*

§ 2. *Involutionen von Flächen.*

Sei β ein Gebiet der Modulfläche M, von dem jeder Punkt n

verschiedene Bildpunkte auf der Fläche F besitzt, P ein solcher erreichbarer Punkt der Grenze von β, dass auf einem gewissen aus β nach P führenden Wege m der n Bildpunkte gegen den Bildpunkt Q von P konvergieren. Sei j eine auf M in der Nähe von P um P gezogene einfache geschlossene Kurve, k ihr auf F in der Nähe von Q gelegenes Bild. Wenn j hinreichend klein gewählt wird, so ist ein keinem Punkte von j entsprechender, in der Nähe von Q gelegener Punkt von F *entweder* Bildpunkt eines innerhalb j liegenden Punktes von M und lässt sich alsdann ohne Berührung von k mit Q verbinden, *oder* Bildpunkt eines ausserhalb j liegenden Punktes von M, in welchem Falle er sich ohne Berührung von k aus der Nähe von Q entfernen lässt. Weil mithin k auf F *zwei und nur zwei Gebiete* bestimmt, so ist k eine einfache geschlossene Kurve, auf welcher die gegebene Involution von F eine Involution mit j als Modullinie bestimmt, deren Ordnung notwendig $= m$ sein muss, so dass sie einer m-periodischen Rotationsgruppe topologisch äquivalent ist. Hieraus folgt unmittelbar, *erstens*, dass die Bildpunkte der erreichbaren Punkte der Grenze von β, mithin auch diese erreichbaren Punkte selbst isoliert sind, dass also diejenigen Punkte von M, welche weniger als n Bildpunkte besitzen, ebenso wie die entsprechenden Bildpunkte selbst, isoliert sind, *zweitens*, dass *die Fläche F eine über die Modulfläche M n-blättrig ausgebreitete Riemannsche Fläche darstellt.*

§ 3. *Endliche Gruppen von Linien.*

Wir betrachten eine endliche Gruppe G von n eineindeutigen und stetigen Transformationen mit invarianter Indikatrix einer Linie F. Weil jede Transformation von G periodisch ist, so muss F notwendig geschlossen sein und kann für keine Transformation von G ein invarianter Punkt existieren. Sei nun s ein Segment von F, von dem der eine Endpunkt S_1 durch die Transformation t von G in den anderen Endpunkt S_2 übergeht, das aber übrigens kein Paar für G äquivalenter Punkte enthält. Seien $S_2, S_3, \ldots S_m, S_{m+1} = S_1$ die Punkte von F, in welche S_1 durch die sukzessiven Potenzen der m-periodischen Transformation t übergeht. Alsdann kann auf keinem Segmente $S_h S_{h+1}$ ausser dem Endpunktepaar ein Paar für G äquivalenter Punkte existieren, so dass zwei Punkte von F nur dann für G äquivalent sind, wenn sie durch eine Potenz von t ineinander übergehen. Weil mithin die Gruppe G ausschliesslich die Potenzen von t enthält, so ist sie einer n-periodischen Rotationsgruppe topologisch äquivalent, d. h. sie ist eine *Involution n-ter Ordnung.*

§ 4. *Endliche Gruppen von Flächen.*

Wir betrachten eine endliche Gruppe G von n eineindeutigen und stetigen Transformationen mit invarianter Indikatrix einer geschlossenen zweiseitigen Fläche F. Sei P ein für eine Untergruppe γ von G invarianter Punkt, τ eine (offenbar periodische) Transformation von γ. Der Transformation τ von F entspricht eine ebenfalls periodische, einen Bildpunkt von P invariant lassende Transformation der einfach zusammenhängenden Ueberlagerungsfläche von F. Hieraus folgt nach dem *Rotationssatze* von KERÉKJÁRTÓ[1]), dass P auf F eine von für τ invarianten Punkten freie volle Umgebung besitzt, so dass ebenfalls eine volle Umgebung von P auf F existiert, innerhalb deren *keine* Transformation von γ einen Punkt invariant lässt. Wenn wir also in hinreichender Nähe von P eine P in ihrem Innern enthaltende einfache geschlossene Kurve konstruieren, so bestimmt dieselbe zusammen mit ihren von γ erzeugten Bildern eine gleichfalls eine einfache geschlossene Kurve darstellende *äussere Grenze k*, welche von γ in solcher Weise in sich transformiert wird, dass für keine Transformation von γ ein invarianter Punkt auftreten kann. Hieraus folgt unmittelbar, dass γ *von einer einzigen periodischen Transformation t erzeugt wird*. Wenn wir nun das System der für G mit P äquivalenten Punkte mit π bezeichnen, so können wir, indem wir t in obiger Weise auf die einfach zusammenhängende Ueberlagerungsfläche von F ausdehnen, mittels des Rotationssatzes weiter folgern, dass in der Menge der Systeme von für G äquivalenten Punkten von F eine volle Umgebung von π existiert, welche sich inklusive π eineindeutig und stetig auf ein Flächenstück abbilden lässt. Hiermit hat sich herausgestellt, dass die Gruppe G eine (übrigens spezielle) *Involution n-ter Ordnung* darstellt.

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[1]) Mathem. Annalen 80, S. 36—41.

Physiology. — *"On the Photo-electricity of Gels."* By Prof. H.
Zwaardemaker and F. Hogewind.

(Communicated in the meeting of February 22, 1919).

When light is allowed to fall on a metal disc, possessing a negative
charge, the disc will be discharged. Not, however, when the disc
is charged positively.

This phenomenon was first discovered and described by **W.**
Hallwachs [1]) in 1888 and is known as "Hallwachs effect".

Afterwards the discharge appeared to be due to an emission of
electrons under the influence of light, notably ultraviolet light. For
this reason a luminous source rich in ultraviolet rays, is to be preferred
for this experiment, e.g. an arc-lamp carbon, whose light falls on
the metal disc either directly or with the aid of quartz-lenses. The
lamp was completely insulated by an amber rod and connected with
an earthed electroscope, which had been charged negatively.

With a view to ward off the inhibitory influence of the electrons
taken up in the air in front of the disc, a wire-work of oxidized
iron-gauze, which is only slightly sensitive, is placed before the metal
disc at a distance of about $1\frac{1}{2}$ cm. This wirework is charged positively
up to a potential of from 50 to 100 volts, and immediately catches
up the electrons emitted.

The light is transmitted through the network to the disc. The
electroscope at once begins to discharge itself. The rate of this
discharge, measured by the so-called half-way time, furnishes an
index for the photo-electrical sensitiveness of the disc.

According to Hallwachs the following materials are responsive
to photo-electricity:

1. Metals. Most of all alkalimetals. Then follow Al, Mg, Zn, etc.
2. Many metallic compounds: oxides, chlorides, bromides, etc.
3. Many minerals.
4. Many dyes, e.g. anilin-dyes; *also* their aqueous solutions.
5. Some insulators, such as sulphur, solid rubber.

Gases become active through the extreme ultraviolet rays.

Among the materials that proved to be inactive are water, stone,
granite, wood.

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[1]) Marx, Handb. der Radiologie. Hallwachs, Lichtelektricität 1915. Bd. IIIb.
S. 245.

Broadly speaking all the solids that absorb light sufficiently and are good conductors of electricity, become photo-electrical.

On the other hand liquid substances, according to HALLWACHS are none of them very active. He found only two liquids distinct in their positive reaction to radiation, viz. anilin and formic acid.

Nor does the literature make mention of liquids as being distinctly photo-electric.

Both the liquids just mentioned belong to the odorous substances and we succeeded in detecting among this category of materials several that were photo-electric in the liquid state, amongst others the liquid terms of the anilin series; toluidin and xylidin. Also guaiacol, cressol, eugenol, anethol, etc. The sensitivity of anethol e.g. comes near to that of the most active metals.

Aqueous *solutions* of all the above solid and liquid substances generally proved not to be photo-electrical. An exception was formed by the solutions of anilin dyes, mentioned before.

This was supposed [1]) to be the consequence of the formation of a pellicle on the surface, constituting a very thin layer of solid matter. Photoelectricity rises in proportion to the thickness of the layer to a certain optimum. This superficial pellicle is connected with the colloidal state of the dye-solution. Oxidation does not come into play here. Inorganic colloids such as arsenic and antimonium-trisulphide act likewise [2]).

However, HALLWACHS himself already records that the photoelectric sensitivity is not always associated with, nor runs parallel with the formation of this pellicle.

In our investigation of odorous substances we found out that a solution of any substance, whether solid or liquid, is photo-electrical only when the three following conditions are satisfied:

1. The dissolved substance must be photo-electric.

2. The solution must largely absorb ultraviolet light.

3. The solution must be colloidal.

In these experiments with liquid substances and with solutions we used filterpaper saturated with the liquid and suspended on a stand that had been insulated by amber.

Filterpaper when having been kept carefully shut off from all contact, shows only little sensitiveness for photo-electricity. However, through adsorption of odorous substances it soon becomes sensitive

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[1]) ROHDE (Ann. der Physik, 19, p. 935—959, 1906).

[2]) PLOGMEIER, Deutsche Phys. Gesellschaft, Verh. 11, p. 382—396 (1909).

and, therefore, should not be kept in an atmosphere laden with odorous matter.

If, moreover, due care is taken to keep in all experiments the same distance from the source of light to the paper and the same area of the lighted surface of the paper, then the half-way time of the electroscope affords a reliable index for the sensitivity of the liquids.

The colloidal state is a conditio sine qua non for the photo-electricity of solutions, which will increase with the growth of the micellae, while the solution is still for some time stationary.

A saturated aqueous solution of eugenol e.g. yields:

	Half-way-time.	
	Lighted	Not lighted
fresh	2 min. 15 sec.	18 min.
after 1 hr.	1 „ 40 „	18 „
„ 2 days	1 „ 15 „	18 „
„ 4 „	1 „	18 „
„ 7 „	50 sec.	18 „
„ 10 „	50 „	18 „

For longer periods the sensitivity keeps constant, if there is an excess of eugenol.

In the same way also various physiological liquids were examined. This inquiry also showed that:

1. Crystalloid solutions are not photo-electrical.

2. Colloidal solutions are so, only if they fulfil the above-mentioned three conditions.

The following materials appeared to be responsive to photo-electricity:

	Half-way-time.	
	Lighted	Not lighted
Serum-globulin sol. (weak)	8 min.	18 min.
Serum-albumin sol. (weak)	8 „	18 „
Horse's blood serum	$5^1/_2$ „	18 „
Horse's blood	$5^1/_2$ „	18 „
Horse's blood hemolysed by water	$3^1/_2$ „	18 „
Hen's eggwhite in glycerine (sat.)	8 „	18 „
Nuclein (sat. aqueous sol.)	7 „	18 „

It appears then that the sensitivity of physiological solutions is moderate.

That of ferments is still smaller:

Pepsin glycerin (sat.)	10 min.	18 min.
Diastase ,, ,,	8 ,,	18 ,,
Pancreatin 2 $\%$ aq. sol.	8 ,,	18 ,,
Leucin 2 $\%$ aq. sol.	10 ,,	18 ,,
Tyrosin sat. aq. sol.	7 ,,	18 ,,

The following appeared to be irresponsive:

Lecithin (sat. aq. sol.) and Casein (sat. aq. sol.), these materials being neither sensitive to photo-electricity of themselves.

The literature does not make mention of the *Hallwachs* effect on *gels*.

We examined a series of gels and found sensitivity with some, with others we did not.

Of the first category the pure substance was also sensitive when thoroughly dried and showed a powerful absorption of ultra-violet rays.

A positive reaction was observed with:

	Half-way-time	
	Lighted	Not lighted
2 $\%$ Agarsolution	9 min.	18 min.
6 $\%$,,	8 ,,	18 ,,
8 $\%$,,	$7^1/_2$,,	18 ,,
2 $\%$ Gelatin sol.	6 ,,	18 ,,
Carragheen	7 ,,	18 ,,
Ichthyocolla	$7^1/_2$,,	18 ,,
Rubber (sheet)	7 ,,	18 ,,
,, (plastic)	10 ,,	18 ,,
,, (vulcanized)	5 ,,	18 ,,

Physiological substances occurring in tissues partly in the gel-condition, we tried to make a model imitative of that tissue. We believe we have found it in a silicic acid gel, prepared by Prof. BEYERINCK's method:

10 c.c. of Na silicate, diluted with twice its volume of water is shaken well and rapidly with 10 c.c. of normal hydrochloric acid, and subsequently poured out into a Petri's dish, where soon after a gel is formed, which is insensitive.

Now if some colloidal solution is poured over the plate before the mass has become quite firm, the gel-mass will be more or less deeply imbibed, together with the liquid.

The solution may also be treated with silicic acid gel before

hydrochloric acid is added to it, so that the whole mass contains the colloidal substance.

Now if the latter is sensitive to photoelectricity, the silicic acid disc has become so too, either only superficially if prepared on the first method, or throughout, if prepared by the 2nd method.

In this manner we found with the following physiological substances:

		Lighted	Not lighted
Silicic acid disc + serum-albumin (weak sol.)		9 min.	18 min.
,, + serum-globulin ,, ,,		9 ,,	18 ,,
,, + lecithin sol. (sat.)		18 ,,	18 ,,
,, + horse's blood		5 ,,	18 ,,
,, + Casein sol. (sat.)		18 ,,	18 ,,
,, + Pancreatin 2 °/₀		9 ,,	18 ,,
,, + lecithin + chloroform		18 ,,	18 ,,
,, + sat. fresh aq. nuclein sol.		7 ,,	18 ,,
,, + sat. fresh tyrosin sol.		6 ,,	18 ,,

If the gel, just described, is saturated with a crystalloid solution, not a vestige of photo-electricity is noticeable.

Converted beforehand to the colloidal state the molecules are apparently spread as a continued layer on and in the gel in order to furnish the violet light with an adequate point of application for its photo-electrical action.

When the thickness of the silicic acid gel is made to be about 2 or 3 m.m. and the colloidal solution is poured out over the surface turned towards the light, a weak photo-electricity will be observed also on the surface that is turned away from the light, apparently because the slow electrons, swarming from the light, are strong enough to penetrate through the gel. When, however, the colloidal solution is poured out over the surface turned away from the light, the hindmost layer remains insensitive, as the light cannot reach it. It is checked by the silicic acid. Neither water nor glycerin check the light appreciably in such thin layers.

By addition of eosin we have endeavoured to utilize the light that penetrates, however without success for photo-electricity, which is not surprising since visible light is not generally capable of arousing photo-electricity (except in alkali-metals, and cleansed aluminium, magnesium and zinc).

The object of our gel-experiments has been to procure a model of an animal tissue, with which we might be able to perform typical experiments on the action of light. The silicic acid gel is particularly adapted for this purpose, as, contrary to the gelatin- and agar-gels,

it is itself entirely destitute of any sensitivity for photo-electricity. This renders it possible to permeate it with all sorts of colloids occurring in the animal tissue and to observe the effect of light on these colloids in divers diffusion and under different conditions. Only the slight permeability of the silicic acid for ultraviolet light is in some respects an impediment. For a deeper penetration of the ultra-violet light silicic acid must be replaced by a gelatin gel, which is itself, as already observed, little sensitive to light. Conversely, covering the gel with a superficial culture will act like a screen. This was evident when e.g. we covered a gelatin gel with a closely plated culture of luminous bacteria. The result was a distinct decrease in the sensitivity to photo-electricity of the gelatin gel.

Our conclusion is that the photo-electricity of animal tissues depends on the sols, gels and solid substances (fibers producing double refraction, crystals, liquid crystals) contained in it. The experiment with the gels affords an opportunity of combining these component parts in any given quantity. If only an effect on the superficial layers is aimed at, silicic acid must be resorted to, as it has of itself no sensitiveness for photo-electricity; while gelatin must be used if the inquirer has in view the effect upon the deeper layers.

Physiology. — *"The measurement of Chronaxia"*. By Prof. J. K. A. WERTHEIM SALOMONSON.

HOORWEG's law for the stimulation of excitable tissues by means of electric currents states that the rate of excitation rapidly lessens during the flow of the current. His law may be mathematically expressed by

$$y = a \int_0^\infty \varphi(t)\, \varepsilon^{-\beta t}\, dt \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

if y represents the excitation caused by a current $I = \varphi(t)$, a and β being constants. HOORWEG calls a the initial constant, β the extinction constant. The reciprocal of the latter $\dfrac{1}{\beta}$ is generally called the time constant of the stimulated tissue. LAPICQUE introduced the word chronaxia to designate this time constant.

The measurement of the chronaxia is of the greatest importance if we wish to indicate the excitability by electricity of the animal tissue. According to DOUMER we can calculate it from the results of three condenser discharges under definite conditions. HOORWEG proposed two condenser discharges and one stimulation with the direct constant current, which for a long time has been the only available method. CLUZET uses a series of discharges of condensers of different capacity and calculates the chronaxia from the one in which the smallest amount of electrical energy was needed to obtain a minimal contraction. LAPICQUE has published a method for directly measuring the chronaxia with the direct current, closing and opening the circuit with two rapidly working contact keys of an instrument called a chronaximeter. A similar method was used by KEITH, ADRIAN and others. I worked out a method in which a calibrated induction coil was used.

In all these measurements we find not only the chronaxia, but also the *rheobasis*, a constant which received this name from LAPICQUE. It is the smallest direct current causing a minimal muscle twitch, and is equal to the quotient of HOORWEG's constants $\dfrac{\beta}{a}$.

When the rheobasis and the chronaxia are known we find from them Hoorweg's initial constant a, or its reciprocal value $\dfrac{1}{a}$ as *quantity constant*.

It is generally much less important to know the rheobasis than the chronaxia. The latter seems to be a true constant, whereas the rheobasis depends on the surface of the electrodes, the place where they are applied, the condition of the skin, and even on the duration of the constant current, used in measuring it. With the same electrodes I found it in one case to be 4.4 milliampere with the condensor method, 6.1 milliampere with the induction coil-method, against 2.6 milliampere as measured with the constant current, the three measurements being made immediately one after the other. But in all three cases the chronaxia came out as 0.00008 second. It seems possible that also differences in the resistance of the body might be responsible for the differences in the rheobasis.

The rheobasis is easily determined and is even a matter of routine work in neurological praxis. But little attention if any is given to the chronaxia. Only if the methods are simplified there may be some chance of a more extensive use of this way of stating the excitability of muscular tissue and motor nerves. Below I give two simplified methods for directly measuring the chronaxia, either by two condensor-discharges or by two measurements with an ordinary not-graduated induction coil. In every case the chronaxia is found without any calculation or with merely one division.

Condensor-method.

Muscles and nerves respond in the same way to discharges of condensers of different capacity C if the Voltage V in each individual case be

$$V = \frac{\beta}{a} R + \frac{1}{aC} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which R is the resistance of the circuit, β and a the above-mentioned constants. This relation was found by Hoorweg. It may be calculated from (1) by putting

$$q(t) = \frac{V}{R} \varepsilon^{-\frac{t}{Rc}}$$

which is the well-known formula for a condensor discharge through a non-conductive resistance. If the expression is integrated and we take for y a unity-effect $= 1$ we get formula (2).

We first make a measurement with a capacity C_1 and find a voltage V which first gives a minimal contraction. Next we take

another somewhat larger capacity C_2 and without modifying V but by putting a resistance W into the circuit we again obtain a minimal contraction.

We then put:

$$\beta R + \frac{1}{C_1} = \beta (R + W) + \frac{1}{C_2}$$

or

$$\frac{1}{\beta} = W \frac{C_1 C_2}{C_2 - C_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We may take for C_2 any capacity larger than C_1. By taking $C_2 = 2C_1$ we get the extremely simple expression for $\frac{1}{\beta}$:

$$\frac{1}{\beta} = W C_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or the chronaxia is the product of the resistance W and the capacity C_2.

If we can use a complete set of graduated condensors we might use a fixed resistance W and try to find the value of C_2 giving a minimal contraction, using formula (3). But as a matter of fact we find the use of a calibrated rheostat more convenient, especially as it allows of the use of formula (4), which is simpler. In this case only two condensors of say 0.05 or 0.1 μF and a rheostat up to 10000 Ohm are necessary; whereas in the first method a set of condensors from 0.001—0.5 μF and a fixed resistance W of 1000 or 2000 Ohm would be required.

The actual measurement of the Voltage V is unnecessary.

Induction coil method.

The secondary discharge of a medical induction coil may be represented by

$$l_{11} = q(t) = I_1 \frac{M}{L_{11}} \varepsilon^{\frac{R_{11}}{L_{11}} t} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in which I_1 is the primary current, M the mutual induction coefficient, L_{11} the selfinduction and R_{11} the resistance of the secondary circuit.

Putting $\varphi(t)$ in HOORWEG's formula (1) we get

$$\eta = \alpha I_1 \frac{M}{L_{11}} \int_0^\infty \varepsilon^{-\left(\frac{R_{11}}{L_{11}} + \beta\right)t} \, dt = \frac{\alpha I_1 M}{R_{11} + \beta L_{11}}$$

and taking $\eta = 1$ we get:

$$\alpha I M = R_{11} + \beta L_{11} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

We now make again two measurements of a minimal contraction. In the first one we insert a selfinduction L into the secondary

circuit and by varying either the primary current strength or more conveniently the coil distance we finally get a minimal contraction. Now leaving the coil distance and the primary current unchanged we take away the added selfinduction L and put in its place a rheostat from which so much resistance is unstopped till the minimal contraction appears again. Then we have:

$$a\,I_1\,M = (R_{11} + W) + \beta L_{11} = R_{11} + \beta\,(L_{11} + L)$$

or

$$\frac{1}{\beta} = \frac{L}{W} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

giving the chronaxia β as the quotient of a resistance into a selfinduction.

This method can still be applied in two different ways. We can either use a fixed selfinduction and a variable resistance or a fixed resistance and a variable selfinduction. The latter might even be provided with a scale graduated to 10000th parts of a second so as to make it a direct reading instrument. Or if we take 1000 ohms for the fixed resistance, the readings of the graduated scale of the induction variometer in Henry will give the value of the chronaxia in 1000th parts of a second.

The advantage of the induction coil method may be gathered from the fact that the combination of a rheostat and graduated selfinduction coil may be used with any medical coil and with any ordinary interrupter. The only restriction to be made is against the use of a secondary coil with less than 3000 windings. The formula used ceases to be accurate as soon as an extremely large resistance is inserted in the secondary circuit. With secondary coils of only a few hundred secondary windings this is already the case with a total secondary resistance of perhaps 1000 ohms. But with coils of more than 3000 windings the secondary resistance may be increased up to 15000 or 20000 Ohms without any appreciable error. The error in these cases is caused by the presence of capacity in the secondary coil, the influence of which is to lower the initial strength of the secondary discharge and to render the calculated chronaxia a trifle too small. But with coils of more than 3000 turns this error is considerably smaller than the error of the measurement itself, as was proved by a special physiological and oscillographic investigation.

Finally I wish to add that with the condenser or the induction coil it is possible to arrange for the use of an ungraduated but variable resistance and a special ohmmeter, which may be graduated for the chronaxia to be directly read on the scale.

Astronomy. — *"Theory of Jupiter's Satellites.* I. *The intermediary orbit"*. By Prof. W. DE SITTER.

(Communicated in the meeting of March 29, 1919).

The following pages contain the elaboration of the theory which was outlined in my paper[1]) of 1918 March 23. Only the results will be given here; the computations will be published in detail in the Annals of the Observatory at Leiden. The present paper gives the determination of the intermediary orbit. As has been explained in the "Outlines", the motion of the satellites is thereby represented as a keplerian ellipse with the constant semi-axis a_i and excentricity e_i, the perijoves having the common retrograde motion $-\varkappa\tau$.

Instead of the time we use the independent variable τ, i.e. we count the time in units of 1.1221899034 mean solar days. The unit of mass is the mass of Jupiter, and the unit of length has been so chosen that the Gaussian constant $f = 1$. This unit of length is

$$a_0 = 0.0070854378 \text{ astronomical units.}$$

The adopted masses of the satellites are[2]):

$$m_1 = 0.00003796 \ (1 + \lambda_1)$$
$$m_2 = 0.00002541 \ (1 + \lambda_2)$$
$$m_3 = 0.00008201 \ (1 + \lambda_3)$$
$$m_4 = 0.00004523 \ (1 + \lambda_4).$$

The mass of the sun is $M = 1047.40 \ (1 + \Sigma \, m_i)$, or

$$M = 1047.600$$

For the quantities J and K depending on the ellipticity, we take

$$J = 0.02186^5 \ (1 + \lambda_0) \qquad K = 0.00259 \ (1 + \lambda_5).$$

These occur exclusively in the combinations Jb^2 and Kb^4 respectively, of which the adopted values expressed in our units are

$$log \ Jb^2 = 5.9969318 - 10$$
$$log \ Kb^4 = 2.72766 - 10.$$

The mean distance of Jupiter from the sun, expressed in our unit, is

$$log \ A = 2.865871.$$

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[1]) Outlines of a new theory of Jupiter's satellites, these Proceedings Vol XX, p. 1289.

[2]) See Annalen van de Sterrewacht te Leiden, Deel XII, Eerste Stuk, Appendix.

The mean anomalies of the satellites in the intermediary orbit are

$$l_i = c_i \tau$$

and the mean longitudes are

$$\lambda_i = \lambda_{00} + \pi_{i_0} + (c_i - \varkappa)\tau$$

where λ_{00} is the longitude of the opposition of II and III, which is taken as origin, and

$$\pi_{10} = \pi_{30} = \pi_{40} = 0, \qquad \pi_{20} = 180°.$$

We have

$$c_1 = 4$$
$$c_2 = 2$$
$$c_3 = 1$$
$$c_4 = 0.43697298$$
$$\varkappa = 0.0144839248.$$

The values of $c_i, \varkappa$, M and A are considered as absolutely exact and not subject to correction. The corrections λ_i to the adopted masses and ellipticity are included explicitly in the formulas.

The perturbative function is given by the formula[1]) (15). This is developed to a series of the form:

$$R = -\tfrac{1}{2} \frac{(c_i - \varkappa)(1 - \mu_i)}{1 + m_i} \Sigma (C_i)_q^n \, e_i^n \cos q l_i$$

$$+ \tfrac{1}{2} \frac{(c_i - \varkappa)(1 - \mu)}{1 + m_i} \Sigma_j \frac{a_i}{a_j} m_j \Sigma \Pi_{q,q'}^{n,n'} (b_{i\,j})_p \, e_i^n \, e_j^{n'} \cos(p\lambda_j - p\lambda_i + q l_i + q' l_j)$$

$$- \frac{(c_i - \varkappa)(1 - \mu_i)}{1 + m_i} \Sigma_j \frac{a_i^2}{a_j^2} m_j \Sigma Q_{q,q'}^{n,n'} \, e_i^n \, e_j^{n'} \cos(\lambda_j - \lambda_i + q l_i + q' l_j)$$

The upper line of this formula contains the terms depending on the ellipticity of the planet and on the indetermined parameter μ_i. I will call this part the "additional" part of the perturbative function. It contains the elements of the perturbed satellite only.

The second line is the principal part of the perturbative function. It has been written down for the case of an inner satellite perturbed by an outer one, i.e. for $j > i$. If the perturbed satellite is the outer one, i.e. if $i > j$, then the factor a_i/a_j must be omitted, and $\Pi_{q,q'}^{n,n'} (b_{ij})_p$ must be replaced by $\Pi_{-q',-q}^{n',n} (b_{ji})_p$. The $\Pi_{q,q'}^{n,n'}$ are the well known operators of NEWCOMB and $(b_{ij})_p$ are the coefficients of LAPLACE in the development of a'/Δ.

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[1]) These Procedings Vol XX, page 1298.

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The third line contains the complementary part of the perturbative function. The coefficients $Q_{q,q'}^{n,n'}$ differ from those of the usual development by the introduction of the terms with J_j and K_j. The values of $(C_i)_q^n$ and $Q_{q,q'}^{n,n'}$ have been given in Leiden Annals XII, 1, pages 22 and 23.

For the determination of the intermediary orbit we only use the non-periodic part $[R_i]$ of the perturbative function. We add to this those terms of the secular part of the perturbative function corresponding to the action of the sun, which do not contain angular elements of the sun. These are with sufficient approximation

$$\frac{(c_i-\varkappa)\,(1-\mu_i)}{1+m_i}\frac{a_i^3}{A^3}\,M\,[\tfrac{1}{4} - \tfrac{3}{8}\,i_\omega^2 + \tfrac{3}{8}\,(e_i^2+e_0^2)],$$

where e_0 is the excentricity and i_0 the inclination of the sun's orbit.

The perturbative function is developed in powers of e_i. For this reason I have also, instead of η_i, taken as unknown $e_i = \eta_i \sqrt{1-\tfrac{1}{4}\eta_i^2}$. The equations determining μ_i and e_i then become, instead of (18) and (19):

$$a_i\,\frac{\partial\,[R_i]}{\partial\,a} + \tfrac{1}{4}\varkappa\,e_i^2 = 0$$

$$\sqrt{1-e_i^2}\,\frac{\partial\,[R_i]}{\partial\,e_i} + \varkappa\,e_i = 0$$

If we denote by $\lfloor R'_i \rfloor$ the non-periodic terms of the principal and complementary parts of the perturbative function, these equations become

$$\frac{\mu_i}{1-\mu_i} - [J_i + \tfrac{1}{2}\,K_i] - (\tfrac{2}{3}\,J_i + \tfrac{5}{2}\,K_i)e_i^2 + \tfrac{1}{2}\,\frac{M}{1+m_i}\frac{a_i^3}{A^3} +$$

$$+ \frac{\varkappa\,e_i^2}{4\,(c_i-\varkappa)\,(1-\mu_i)} + \frac{1}{(c_i-\varkappa)\,(1-\mu_i)}\,a_i\,\frac{\partial\,[R'_i]}{\partial a_i} = 0 \quad . \quad . \quad (1)$$

$$A_i\,e_i + 2\,(c_i-\varkappa)\,(1-\mu_i)\,J_i\,e_i^3 + (1-\tfrac{1}{2}\,e_i^2)\,\frac{\partial\,[R'_i]}{\partial e_i} = 0 \quad . \quad . \quad (2)$$

$$A_i = \varkappa + (c_i-\varkappa)\,(1-\mu_i)\,(J_i+K_i) + \tfrac{3}{4}\,\frac{(c_i-\varkappa)\,(1-\mu_i)}{1+m_i}\,M\,\frac{a_i^3}{A^3}.$$

The first equation gives $\mu'_i = \dfrac{\mu_i}{1-\mu_i}$. Then we find a_i from

$$a_i^2\,(c_i-\varkappa)^2 = (1+m_i)\,(1+\mu_i').$$

For the solution of the equations (1) and (2) we started from the approximations [1])

$$\log a_1 = 9.5997740 - 10 \qquad e_1 = 0.00404164$$
$$\log a_2 = 9.8015496 - 10 \qquad e_2 = 0.00936330$$
$$\log a_3 = 0.0042524 \qquad e_3 = 0.00059680$$
$$\log a_4 = 0.2494696 \qquad e_4 = 0$$

The coefficients of LAPLACE corresponding to these values of a_i were derived from those given by SOUILLART by the application of the corrections necessary to reduce from SOUILLART's values of the ratios of the mean distances to ours. Then with these coefficients the NEWCOMB's operators occurring in the formulas (1) and the other coefficients of these formulas were computed, and the values of μ'_i were solved and from these the values of a_i were derived. The coefficients of LAPLACE were then reduced to these new values of a_i, and a second approximation of μ'_i was derived, which differed only very little from the first. The corresponding values of a_i were considered as final, and were used as the basis for an entirely new computation of the LAPLACE coefficients. Then with these coefficients we computed the operators necessary for the equations (2). These equations (2) are not, like (1), independent of each other, but must be solved by successive approximations. The approximations, which converged very rapidly, were continued until the ninth decimal place of e_i was no longer affected. The values of e_i thus derived are the definitive ones. They were substituted in (1) instead of the original approximations, but this did not produce any change in the values of μ'_i and a_i.

The elements of the intermediary orbit are thus determined. The different terms of μ'_i are given below. The terms marked *"add"* are the second and third of the formula (1), *"$\varkappa$"* is the fifth and *"sun"* the fourth term. The effect of the last term is given for each perturbing satellite separately. The quantities $\varkappa$ and e_i are considered to be of the first order, the masses and J_i are of the second order. A term containing the factor me^2 is thus of the fourth order. We found [2])

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μ'_1 : *add.* : 2nd order $+$ ·000 62824 $\Big\}$ $+$ ·000 62826

         4th ,, $+$ 2

$\varkappa$: 3rd ,, $-$ 3

sun : 3rd ,, $-$ 8

m_2 : 2nd ,, $-$ ·000 00552

     3rd ,, $+$ 48 $\Big\}$ $-$ 507

     4th ,, $-$ 3

m_3 : 2nd ,, $-$ 303

m_4 : 2nd ,, $-$ 27

$$\mu'_1 = +\ ·00061977$$

μ'_2 : *add.* : 2nd order $+$ ·000 24791 $\Big\}$ $+$ ·000 24794

         4th ,, $+$ 3

$\varkappa$: 3rd ,, $-$ 32

sun : 3rd ,, $-$ 34

m_1 : 2nd ,, $+$ ·000 05599

     3rd ,, $-$ 281 $\Big\}$ $+$ 5328

     4th ,, $+$ 10

m_3 : 2nd ,, $-$ ·000 01761

     3rd ,, $+$ 157 $\Big\}$ $-$ 1609

     4th ,, $-$ 5

m_4 : 2nd ,, $-$ 119

$$\mu'_2 = +\ ·000\ 28328$$

μ'_3 : *add.* : 2nd order $+$ ·000 09739

 sun : 3rd ,, $-$ 136

 m_1 : 2nd ,, $+$ 4313

 m_2 : 2nd ,, $+$ ·000 03738

     3rd ,, $-$ 114 $\Big\}$ $+$ 3628

     4th ,, $+$ 3

 m_4 : 2nd ,, $-$ 643

$$\mu'_3 = +\ ·000\ 16901$$

μ'_4 : *add.* : 2nd order $+$ ·000 03148

    sun : 3rd ,, $-$ 741

    m_1 : 2nd ,, $+$ 3946

    m_2 : 2nd ,, $+$ 2816

    m_3 : 2nd ,, $+$ 11069

$$\mu'_4 = +\ ·000\ 20238$$

From these we find

$$\log a_1 = 9.559\ 77215 - 10 + \delta \log a_1$$
$$\log a_2 = 9.801\ 46241 - 10 + \delta \log a_2$$
$$\log a_3 = 0.004\ 26052 \qquad + \delta \log a_3$$
$$\log a_4 = 0.249\ 49217 \qquad + \delta \log a_4$$

The corrections $\delta \log a_i$ have been added to take account of eventual corrections λ_i to the masses and to J and K. We also put

$$e_i = e_{i_0} (1 + \eta_i)$$

Then we have

$$10^7\ \delta \log a_1 = +\ 907\ \lambda_0 + \quad 2\ \lambda_5 + 55\ \lambda_1 - \quad 7\ \lambda_2 - 4\ \lambda_3$$
$$10^7\ \delta \log a_2 = +\ 359\ \lambda_0 + 77\ \lambda_1 + 22\ \lambda_2 - \quad 22\ \lambda_3 - 2\ \lambda_4 - \eta_1 - \eta_2$$
$$10^7\ \delta \log a_3 = +\ 140\ \lambda_0 + 62\ \lambda_1 + 52\ \lambda_2 + 119\ \lambda_3 - 9\ \lambda_4 - \eta_2$$
$$10^7\ \delta \log a_4 = +\ \ 45\ \lambda_0 + 57\ \lambda_1 + 41\ \lambda_2 + 160\ \lambda_3 + 66\ \lambda_4$$

For the coefficients A_i of the first term of the equations (2) we find

	I	II	III	IV
$\varkappa$	0·014 48392	0·014 48392	0·014 48392	0·014 48392
add.	2 50655	49242	9599	1330
sun	50	100	201	469
A_i	0·016 99007	0·014 97735	0·014 58193	0.014 50191

The second term can be neglected for the satellites III and IV. For I and II it contributes -2 and -5 respectively to the eighth decimal place of e_i.

The third term gives

$$10^{10} (1 - \tfrac{1}{2} e_1{}^2) \frac{\partial [R'_1]}{\partial e_1} : m_2 : \text{2nd order} - 752429$$

	3rd ,, + 43589	
	4th ,, — 1908	— 710677
	5th ,, + 73	
	6th ,, — 3	
m_3 : 3rd ,, + 801		+ 793
4th ,, — 7		
m_4 : 3rd ,,		+ 70
		— 709814

$$10^{10}\left(1 - \tfrac{1}{2}e_2{}^2\right)\frac{\partial\,[R'_2]}{\partial e_2} : m_1 : \text{2nd order} - 312553$$

$$\text{3rd} \quad ,, \quad + \quad 72951$$
$$\text{4th} \quad ,, \quad - \quad 3396$$
$$\text{5th} \quad ,, \quad + \quad 125$$
$$\text{6th} \quad ,, \quad - \quad 3$$

$$\left.\right\} \quad - \ 242876$$

$$m_2 : \text{2nd order} - 1198671$$
$$\text{3rd} \quad ,, \quad + \quad 42122$$
$$\text{4th} \quad ,, \quad - \quad 930$$
$$\text{5th} \quad ,, \quad + \quad 18$$

$$\left.\right\} \quad - \ 1157462$$

$$m_4 : \text{3rd} \quad ,, \qquad\qquad + \qquad 368$$
$$\overline{\qquad\qquad\qquad - \ 1399970}$$

$$10^{10}\left(1 - \tfrac{1}{2}e_3{}^2\right)\frac{\partial\,[R'_3]}{\partial e_3} : m_1 : \text{3rd order} - \quad 75$$
$$\text{4th} \quad ,, \quad + \quad 4$$

$$\left.\right\} \quad - \qquad 72$$

$$m_2 : \text{2nd} \quad ,, \quad - \ 100444$$
$$\text{3rd} \quad ,, \quad + \quad 13874$$
$$\text{4th} \quad ,, \quad - \quad 366$$
$$\text{5th} \quad ,, \quad + \quad 7$$

$$\left.\right\} \quad - \qquad 86928$$

$$m_4 : \text{3rd} \qquad\qquad\qquad\qquad + \qquad 77$$
$$\overline{\qquad\qquad\qquad\qquad - \qquad 86923}$$

$$10^{10}\left(1 - \tfrac{1}{2}e_4{}^2\right)\frac{\partial\,[R'_4]}{\partial e_4} : m_1 \ \text{3rd order} \ + \quad 5$$
$$m_2 \ \text{3rd} \quad ,, \quad + \ 51$$
$$m_3 \ \text{3rd} \quad ,, \quad - \ 71$$
$$\overline{\qquad\qquad - \ 15}$$

The terms of the sixth order have not been computed directly, but have been derived by extrapolation of the series of logarithms of the terms of the second to fifth orders.

We find thus:

$$e_1 = 0\cdot004\ 17757\ (1 + \eta_1)$$
$$e_2 = 0\cdot009\ 34720\ (1 + \eta_2)$$
$$e_3 = 0\cdot000\ 59610\ (1 + \eta_3)$$
$$e_4 = 0\cdot000\ 00010\ (1 + \eta_4)$$

The values of η_i are

$\eta_1 = - \ \cdot 14356 \ \lambda_0 - \cdot 00049 \ \lambda_5 - \cdot 00683 \ \lambda_1 + \cdot 98651 \ \lambda_2 - \cdot 03338 \ \lambda_3 -$
$\qquad - \ \cdot 00009 \ \lambda_4 + \cdot 021 \ \lambda_0{}^2 + \cdot 001 \ \lambda_0 \lambda_1 - \cdot 140 \ \lambda_0 \lambda_2 + \cdot 006 \ \lambda_0 \lambda_3 -$
$\qquad - \ \cdot 006 \ \lambda_1 \lambda_2 + \cdot 001 \ \lambda_1 \lambda_3 - \cdot 013 \ \lambda_2{}^2 + \cdot 034 \ \lambda_2 \lambda_3 + \cdot 02 \ \lambda_0{}^2 \lambda_2$

$\eta_2 = - \ \cdot 02951 \ \lambda_0 + \cdot 16326 \ \lambda_1 - \cdot 01272 \ \lambda_2 + \cdot 77826 \ \lambda_3 - \cdot 00024 \ \lambda_4 +$
$\qquad + \ \cdot 001 \ \lambda_0{}^2 - \cdot 002 \ \lambda_0 \lambda_1 + \cdot 002 \lambda_0 \lambda_2 - \cdot 024 \lambda_0 \lambda_3 - \cdot 005 \lambda_1{}^2 + \cdot 010 \ \lambda_1 \lambda_2$
$\qquad + \ \cdot 030 \ \lambda_1 \lambda_3 - \cdot 001 \ \lambda_2 \lambda_3 - \cdot 018 \ \lambda_3^2$

$\eta_3 = - \ \cdot 0023 \ \lambda_0 - \cdot 0215 \ \lambda_1 + \cdot 9878 \ \lambda_2 - \cdot 1068 \ \lambda_3 - \cdot 0008 \ \lambda_4 - \cdot 02 \ \lambda_1 \lambda_2 -$
$\qquad - \ \cdot 01 \ \lambda_2{}^2$

$\eta_4 = + \ 0 \cdot 1 \ \lambda_0 - 1 \cdot 0 \ \lambda_1 + 1 \cdot 0 \ \lambda_2 + 1 \cdot 6 \ \lambda_3 - \lambda_1 \lambda_2 + 2 \ \lambda_2 \lambda_3$

The coordinates in the intermediary orbit are given by the formulas

$$r_i = a_i \ \varrho_i,$$
$$w_i = \lambda_{00} + \pi_{i_0} + (c_i - \varkappa) \ \tau + E_i$$
$$= \lambda_{i_0} + n_i t + E_i,$$

where ϱ_i and E_i are the ordinary elliptic values of the radius-vector and the equation of the centre. We have, in astronomical units:

$$log \ a_1 = 7 \cdot 450 \ \ 13884 - 10$$
$$log \ a_2 = 7 \cdot 651 \ \ 82910 - 10$$
$$log \ a_3 = 7 \cdot 854 \ \ 62721 - 10$$
$$log \ a_4 = 8 \cdot 100 \ \ 30886 - 10$$

From the above values of e_i we find:

$\varrho_1 = \quad 1.000 \ \ 00873$
$\qquad - \ \cdot 004 \ \ 17755 \ cos \ \ 4\tau \qquad E_1 = + \ 0^\circ \cdot 478714 \ sin \ \ 4\tau$
$\qquad - \ \qquad \quad \ 873 \ cos \ \ 8\tau \qquad \quad \ + \qquad \quad 1250 \ sin \ \ 8\tau$
$\qquad - \ \qquad \qquad \ \ 3 \ cos \ 12\tau \qquad \quad \ + \qquad \qquad 5 \ sin \ 12\tau$

$\varrho_2 = \quad 1 \cdot 000 \ \ 04368$
$\qquad - \ \cdot 009 \ \ 34684 \ cos \ 2\tau \qquad E_2 = + \ 1^\circ .071098 \ sin \ 2\tau$
$\qquad - \ \qquad \quad 4368 \ cos \ 4\tau \qquad \quad \ + \qquad \quad 6258 \ sin \ 4\tau$
$\qquad - \ \qquad \qquad 36 \ cos \ 6\tau \qquad \qquad + \qquad \qquad 50 \ sin \ 6\tau$

$\varrho_3 = \quad 1 \cdot 000 \ \ 00018$
$\qquad - \ \qquad 59610 \ cos \ \tau \qquad \ E_3 = + \ 0^\circ \cdot 068308 \ sin \ \tau$
$\qquad - \ \qquad \quad \ \ 18 \ cos \ 2\tau \qquad \qquad + \qquad \qquad 25 \ sin \ 2\tau$

$\varrho_4 = \quad 1$
$\qquad - \ \cdot 000 \ \ 00010 \ cos \ c_4\tau \qquad E_4 = + \ 0^\circ .000012 \ sin \ c_4\tau$

The inequalities in longitude are expressed in degrees. The angle τ is counted from the opposition of II and III on 1899 June 28, $11^h47^m35^s$ Greenwich mean time. (See "Outlines", these Proceedings Vol. **XX**. p. 1299).

Astronomy. — *"On the perturbations in the motion of Hyperion proportional to the first power of Titan's eccentricity"*. By Dr. J. WOLTJER Jr. (Communicated by Prof. W. DE SITTER).

(Communicated in the meeting of March 29, 1919).

1. The object of this paper consists of the computation of those terms in the motion of Hyperion that are proportional to the first power of Titan's eccentricity, under the restrictions mentioned in Chapter II § 1 of the "Investigations" [1]). The arguments of these perturbations are formed by combining the secular part of the difference in longitude of pericentre for the satellites with multiples of the argument of the libration. If this multiple is an odd number, the coefficients in the mean anomaly contain the square root of the disturbing mass as divisor; the value of the corresponding perturbation of the mean anomaly (and mean longitude) can amount to about half a degree. It is obvious to suppose that here we are concerned with those perturbations, which H. STRUVE [2]) mentioned at the conclusion of his discussion of the orbit of Hyperion; their influence clearly was stated by him from observation; according to his estimation their value also could amount to about half a degree.

This paper forms a continuation of the "Investigations" and of "The longitude of Hyperion's pericentre and the mass of Titan" [3]).

2. The terms of the four variables $\varrho, \sigma, \theta, \Omega$, of the first order with respect to Titan's eccentricity, viz. $d\varrho, d\sigma, d\theta, d\Omega$ are determined by the following system of linear differential equations [4]):

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[1]) Investigations in the theory of Hyperion. Here after to be cited as "Investigations."

[2]) Publications de l'Observatoire Central Nicolas. Série II. Vol. XI. Beobachtungen der Saturnstrabanten. St. Pétersbourg. 1898. p. 290.

[3]) Proceedings, Vol. XXI, N⁰. 6 and 7.

[4]) Investigations, p. 48.

$$\frac{d\delta\varrho}{dt} = \frac{\partial^2 R_1}{\partial\theta\partial\varrho}\,\delta\varrho + \frac{\partial^2 R_1}{\partial\theta\partial\sigma}\,\delta\sigma + \frac{\partial^2 R_1}{\partial\theta^2}\,\delta\theta + \frac{\partial R_2}{\partial\theta},$$

$$\frac{d\delta\sigma}{dt} = \frac{\partial R_2}{\partial\Omega},$$

$$\frac{d\delta\theta}{dt} = -\frac{\partial^2(R_0+R_1)}{\partial\varrho^2}\,\delta\varrho - \frac{\partial^2 R_1}{\partial\varrho\partial\sigma}\,\delta\sigma - \frac{\partial^2 R_1}{\partial\varrho\partial\theta}\,\delta\theta - \frac{\partial R_2}{\partial\varrho}, \tag{1}$$

$$\frac{d\delta\Omega}{dt} = -\frac{\partial^2 R_1}{\partial\varrho\partial\sigma}\,\delta\varrho - \frac{\partial^2 R_1}{\partial\sigma^2}\,\delta\sigma - \frac{\partial^2 R_1}{\partial\sigma\partial\theta}\,\delta\theta - \frac{\partial R_2}{\partial\sigma}.$$

In the coefficients of $\delta\varrho, \delta\sigma, \delta\theta$, as well as in the known terms of these differential equations, the values of $\varrho, \sigma, \theta, \Omega$ for $e' = 0$ are to be substituted; further the terms of R_2 of the second order and higher in e' are to be omitted; thus [1]):

$$R_2 = \frac{m'}{a'}\,e'\,[g(\theta)\cos\Omega + h(\theta)\sin\Omega]. \tag{2}$$

The values of $\varrho, \sigma, \theta, \Omega$ for $e' = 0$ are functions of two constants of integration, σ_0 and q, and two linear functions of the time, τ and ϖ, which both contain an additive constant of integration; the formulae for the four variables are [2]):

$$\varrho = \sum_{p=0}^{p=\infty} \varrho_p\,\mu^p, \qquad\qquad \theta = \sum_{p=0}^{p=\infty} \theta_p\,\mu^p,$$

$$\sigma = \sum_{p=0}^{p=\infty} \sigma_p\,\mu^p, \qquad\qquad \Omega = \varpi + \sum_{p=0}^{p=\infty} \Omega_p\,\mu^p, \tag{3}$$

$$\mu = \sqrt{\frac{m'}{M}},$$

where

$$\varrho_p = \sum_{s=0}^{s=\infty} \varrho^{(p,s)}\cos s\tau, \quad \theta_p = \sum_{s=1}^{s=\infty} \theta^{(p,s)}\sin s\tau, \quad \Omega_p = \sum_{s=1}^{s=\infty} \Omega^{(p,s)}\sin s\tau,$$

$$\tau = \nu t + \gamma, \qquad \nu = \mu \sum_{p=0}^{p=\infty} \nu_{p+1}\,\mu^p, \tag{4}$$

$$\varpi = \chi t + \text{const.}, \quad \chi = \mu^2 \sum_{p=0}^{p=\infty} \chi_{p+2}\,\mu^p,$$

and ϱ_0; $\sigma_0, \ldots, \sigma_p, \ldots$; $\theta^{(p,s)}$; $\varrho^{(p,s)}$; $\Omega^{(p,s)}$; ν_p; χ_p; and γ are constant quantities. Deviating from the notation of the "Investigations", the

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[1]) Investigations, p. 22.

[2]) Investigations, p. 23 and Proceedings, Vol. XXI, N°. 6 and 7.

coefficient of t in ϖ has been denoted by χ, to prevent confusion with the known number π. The quantity ϱ_0, occurring in the different coefficients, is a function of σ_0 and q, determined by the relation [1])

$$\frac{\overline{\partial R_0}}{\partial \varrho} + \frac{\overline{\partial R_1}}{\partial \varrho} = -3n'; \tag{5}$$

here the constant term of a periodic function has been denoted by a stroke above the functional sign. The resulting development of ϱ_0 is

$$\varrho_0 = \sum_{p=0}^{p=\infty} l_p \mu^p; \tag{6}$$

l_0 is a constant, $l_1 = 0$; $l_2, \ldots, l_p, \ldots$ are functions of σ_0 and q.

3. Substituting the developments (3) and (4) in (2) we get:

$$R_2 = \frac{m' e'}{M a'} \left[\cos \varpi \sum_{p=0}^{p=\infty} A_p \cos p\tau + \sin \varpi \sum_{p=1}^{p=\infty} B_p \sin p\tau \right], \;\Big|$$

$$A_p = \sum_{r=0}^{r=\infty} A_{p,r} \mu^r, \qquad B_p = \sum_{r=0}^{r=\infty} B_{p,r} \mu^r; \tag{7}$$

this formula can be written so:

$$R_2 = \frac{m' e'}{M a'} \sum_{-\infty}^{+\infty} C_p \cos (\varpi + p\tau), \tag{8}$$

where

$$C_0 = A_0,$$

$$C_p = \frac{A_p - B_p}{2}, \qquad p \geq 1, \tag{9}$$

$$C_{-p} = \frac{A_p + B_p}{2}, \qquad p \geq 1,$$

and C_p can be developed so:

$$C_p = \sum_{r=0}^{r=\infty} C_{p,r} \mu^r, \qquad p = -\infty, \ldots, +\infty \;. \tag{10}$$

The coefficients $A_{p,r}$, $B_{p,r}$, $C_{p,r}$ are functions of ϱ_0, σ_0, q.

The values of the coefficients $C_{p,0}$ and of the derivatives of these coefficients, considered as functions of ϱ_0, σ_0 and q, with respect to q have been collected in the next table. These values belong to the numerical values of the coefficients of the developments (3) and (4), deduced in the second chapter of the "Investigations".

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[1]) Investigations, Chapter II, § 8.

p	$C_{p,0}\dfrac{10^5}{M}$	$q\dfrac{\partial C_{p,0}}{\partial q}\cdot\dfrac{10^5}{M}$	p	$C_{p,0}\dfrac{10^5}{M}$	$q\dfrac{\partial C_{p,0}}{\partial q}\cdot\dfrac{10^5}{M}$
0	+ 93397	− 1340			
1	+ 18685	+ 20056	− 1	− 18685	− 20056
2	+ 318	+ 712	− 2	+ 318	+ 712
3	− 264	− 826	− 3	+ 264	+ 826
4	− 10	− 42	− 4	− 10	− 42
5	+ 4	+ 20	− 5	− 4	− 20

For the further developments of this paper the value of the coefficient $C_{0,1}$ is required.

We have the equation:

$$\frac{1}{M}\sum_{p=0}^{p=\infty} A_{p,1}\cos p\tau = \left[\frac{\partial g}{\partial \varrho}\right]_0 \varrho_1 + \left[\frac{\partial g}{\partial \sigma}\right]_0 \sigma_1 + \left[\frac{\partial g}{\partial \theta}\right]_0 \theta_1 + [h]_0\,\Omega_1\,, \quad (11)$$

$[\ ]_0$ being an abbreviation for $[\ ]_{\varrho=\varrho_0,\sigma=\sigma_0,\theta=\theta_0}$.

The right member of this formula is an even periodic function of τ; if we replace τ by $\pi-\tau$, $\varrho_1,\sigma_1 (= 0), \theta_1$ and Ω_1 change their sign, their coefficients remaining unaltered; thus the left member is an even periodic function of τ, changing its sign if we replace τ by $\pi-\tau$; then

$$A_{2p,1} = 0, \quad p = 0, 1, \ldots;$$

and

$$C_{0,1} = A_{0,1} = 0 \ . \tag{12}$$

4. As regards $d\theta$ [1]) the solution of the equations (1) is:

$$d\theta = \left[\frac{\partial\theta}{\partial\sigma_0}\frac{\partial\sigma}{\partial q} - \frac{\partial\theta}{\partial q}\frac{\partial\sigma}{\partial\sigma_0}\right]\int\frac{dt}{\Delta}\frac{\partial R_2}{\partial\tau} + \frac{\partial\theta}{\partial\tau}\int\frac{dt}{\Delta}\left[\frac{\partial R_2}{\partial q}\frac{\partial\sigma}{\partial\sigma_0} - \frac{\partial R_2}{\partial\sigma_0}\frac{\partial\sigma}{\partial q}\right]$$

$$+ \frac{d\sigma}{\Delta}\left[\left(\frac{\partial\Omega}{\partial\tau\cdot\partial q}\frac{\partial\theta}{} - \frac{\partial\Omega}{\partial q}\frac{\partial\theta}{\partial\tau}\right)\frac{\partial\sigma}{\partial\sigma_0} + \left(\frac{\partial\Omega}{\partial\sigma_0}\frac{\partial\theta}{\partial\tau} - \frac{\partial\Omega}{\partial\tau}\frac{\partial\theta}{\partial\sigma_0}\right)\frac{\partial\sigma}{\partial q}\right]$$

$$+ \frac{\partial\theta}{\partial\tau}\left[\frac{\partial v}{\partial\sigma_0}\frac{\partial\sigma}{\partial q} - \frac{\partial v}{\partial q}\frac{\partial\sigma}{\partial\sigma_0}\right]\int dt\left[\int\frac{dt}{\Delta}\frac{\partial R_2}{\partial\tau}\right]$$

$$+ \frac{\partial\theta}{\partial\tau}\left[\frac{\partial\chi}{\partial\sigma_0}\frac{\partial\sigma}{\partial q} - \frac{\partial\chi}{\partial q}\frac{\partial\sigma}{\partial\sigma_0}\right]\int\frac{dt}{\Delta}\,d\sigma. \tag{13}$$

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[1]) Investigations, III, § 1.

The quantity Δ is a constant; its value results from the equation

$$\Delta = \left(\frac{\partial \varrho}{\partial \sigma_\bullet}\frac{\partial \theta}{\partial \tau} - \frac{\partial \varrho}{\partial \tau}\frac{\partial \theta}{\partial \sigma_\bullet}\right)\frac{\partial \sigma}{\partial q} - \left(\frac{\partial \varrho}{\partial q}\frac{\partial \theta}{\partial \tau} - \frac{\partial \varrho}{\partial \tau}\frac{\partial \theta}{\partial q}\right)\frac{\partial \sigma}{\partial \sigma_\bullet}. \qquad (14)$$

In (13) and (14) the quantities $\varrho, \sigma, \theta, \Omega, R_2, v, \chi$ are to be considered as functions of $q, \sigma_0, \tau, \varpi$.

In (14) the difference factored by $\dfrac{\partial \sigma}{\partial q}$ can be represented by a power series in μ without constant term; the same is the case with $\dfrac{\partial \sigma}{\partial q}$, only here also the first power of μ fails. Thus:

$$\left(\frac{\partial \varrho}{\partial \sigma_\bullet}\frac{\partial \theta}{\partial \tau} - \frac{\partial \varrho}{\partial \tau}\frac{\partial \theta}{\partial \sigma_\bullet}\right)\frac{\partial \sigma}{\partial q} = \mu^3 \times power\ series\ in\ \mu.$$

Considering the fact that Δ is constant and developing the difference factored by $\dfrac{\partial \sigma}{\partial \sigma_\bullet}$, we get:

$$\Delta = \left[-\mu\frac{\partial \varrho_0}{\partial q}\frac{\partial \theta_1}{\partial \tau} + \mu\frac{\partial \varrho_1}{\partial \tau}\frac{\partial \theta_0}{\partial q} + \mu^2\frac{\partial \varrho_2}{\partial \tau}\frac{\partial \theta_0}{\partial q}\right]_{\tau=\frac{\pi}{2}} + \mu^3 \times power\ series\ in\ \mu.$$

Thus:

$$\Delta = \left[\mu\frac{\partial \varrho_1}{\partial \tau}\frac{\partial \theta_0}{\partial q} + \mu^2\frac{\partial \varrho_2}{\partial \tau}\frac{\partial \theta_0}{\partial q}\right]_{\tau=\frac{\pi}{2}} + \mu^3 \times power\ series\ in\ \mu;$$

in the derivatives occurring in this formula, the quantities $\varrho_1, \varrho_2, \theta_0$ are to be considered functions of ϱ_0, σ_0, q and τ.

Putting $R_1 = \mu^2 F_1$, from the system of equations (A) of Chapter II, § 3, of the "Investigations" we deduce:

$$v_1\frac{\partial \varrho_2}{\partial \tau} = \frac{\partial^2 F_1}{\partial \varrho \partial \theta}\varrho_1 + \frac{\partial^2 F_1}{\partial \theta^2}\theta_1.$$

If $\tau = \dfrac{\pi}{2}$, then $\varrho_1 = \theta_1 = 0$, thus $\left[\dfrac{\partial \varrho_2}{\partial \tau}\right]_{\tau=\frac{\pi}{2}} = 0.$

As

$$\frac{\partial \varrho_1}{\partial \tau} = -\frac{1}{\left[\dfrac{\partial^2 R_0}{\partial \varrho^2}\right]_{\varrho=\varrho_0}}v_1, \qquad \frac{\partial^2 \theta_0}{\partial \tau^2} = -\frac{a_0^2 v_1}{48}\frac{\partial^2 \theta_0}{\partial \tau^2},$$

we get:

$$\Delta = -\mu\frac{a_0^2 v_1}{48}\left[\frac{\partial^2 \theta_0}{\partial \tau^2}\right]_{\tau=\frac{\pi}{2}} + \mu^3 \times power\ series\ in\ \mu;$$

putting:

$$\Delta = \overset{p=\infty}{\underset{p=0}{\Sigma}} \Delta_p \, \mu^p , \qquad (15)$$

we have

$$\Delta_\bullet = 0, \qquad \Delta_1 = + \, 0.0083292 \, \frac{a_0^2 \, \nu_1}{q}, \qquad \Delta_2 = 0 . \qquad (16)$$

5. Denoting the five terms of the right member of (13) by I, II, III, IV, V, each of these terms can be developed thus:

$$\left. \begin{aligned} I &= \overset{+\infty}{\underset{-\infty}{\Sigma}} I_p \, sin \, (\varpi + p\tau), \\ &\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ V &= \overset{+\infty}{\underset{-\infty}{\Sigma}} V_p \, sin \, (\varpi + p\tau). \end{aligned} \right\} \qquad (17)$$

The coefficients $I_p, \ldots, V_p$ have e' as factor and can be developed thus:

$$\left. \begin{aligned} I_p &= \overset{r=\infty}{\underset{r=0}{\Sigma}} I_{p,r} \, \mu^r , \\ II_p &= II_{p,-1} \, \mu^{-1} + \overset{r=\infty}{\underset{r=0}{\Sigma}} II_{p,r} \, \mu^r , \\ III_p &= \overset{r=\infty}{\underset{r=0}{\Sigma}} III_{p,r} \, \mu^r , \\ IV_p &= \overset{r=\infty}{\underset{r=0}{\Sigma}} IV_{p,r} \, \mu^r , \\ V_p &= V_{p,-1} \, \mu^{-1} + \overset{r=\infty}{\underset{r=0}{\Sigma}} V_{p,r} \, \mu^r . \end{aligned} \right\} \qquad (18)$$

The following development for $\delta\theta$ results:

$$\left. \begin{aligned} \delta\theta &= e' \overset{p=\infty}{\underset{p=0}{\Sigma}} \theta_p^{(e')} \mu^p + e' \, \theta_{-1}^{(e')} \mu^{-1} , \\ \theta_p^{(e')} &= \overset{+\infty}{\underset{-\infty}{\Sigma}} \theta_{(e')}^{(p,q)} \, sin \, (\varpi + q\tau), \quad p = -1, 0, .., +\infty . \end{aligned} \right\} \qquad (19)$$

The coefficients $\theta_{(e')}^{(p,q)}$ can be determined by the relations:

$$\left. \begin{aligned} e' \, \theta_{(e')}^{(-1,q)} &= II_{q,-1} + V_{q,-1}, \\ e' \, \theta_{(e')}^{(p,q)} &= I_{q,p} + II_{q,p} + III_{q,p} + IV_{q,p} + V_{q,p} , \quad p = 0, .., +\infty . \end{aligned} \right\} \qquad (20)$$

The development of $\delta\sigma$ is:

$$\delta\sigma = e' \sum_{p=0}^{p=\infty} \sigma^{(e')}_p \mu^p ,$$

$$\sigma^{(e')}_p = \sum_{-\infty}^{+\infty} \sigma^{(p,q)}_{(e')} \cos\,(\varpi + q\tau).$$

(21)

The value of $\delta\varrho$ results from the third equation of (1) without any integration. Thus:

$$\delta\varrho = \frac{1}{\dfrac{\partial^2(R_0 + R_1)}{\partial\varrho^2}} \left\{ -\frac{d\delta\theta}{dt} - \frac{\partial^2 R_1}{\partial\varrho\partial\sigma}\,\delta\sigma - \frac{\partial^2 R_1}{\partial\varrho\partial\theta}\,\delta\theta - \frac{\partial R_2}{\partial\varrho} \right\}.$$ (22)

Then $\delta\varrho$ can be developed so:

$$\delta\varrho = e' \sum_{p=0}^{p=\infty} \varrho^{(e')}_p \mu^p ,$$

$$\varrho^{(e')}_p = \sum_{\infty}^{+\infty} \varrho^{(p,q)}_{(e')} \cos\,(\varpi + q\tau).$$

(23)

According to (1), $\delta\Omega$ results from the equation:

$$\frac{d\delta\Omega}{dt} = - \frac{\partial^2 R_1}{\partial\varrho\partial\sigma}\,\delta\varrho - \frac{\partial^2 R_1}{\partial\sigma^2}\,\delta\sigma - \frac{\partial^2 R_1}{\partial\sigma\partial\theta}\,\delta\theta - \frac{\partial R_2}{\partial\sigma} \quad .$$ (24)

The right member can be developed as a power series in μ; the constant term of this series fails; each coefficient is equal to a sum of terms, each of which contains e' as factor and. is of the form:

$$\text{coefficient.}\ \cos\,(\varpi + p\tau),$$

$p = -\infty, .., +\infty$. The coefficient of μ is equal to:

$$- \frac{Me'}{a'} \left[\frac{\partial^2 f}{\partial\sigma\partial\theta} \right]_{\varrho_0\sigma_0\theta_0} \theta^{(e}_{-1} .$$

As

$$\theta^{(e)}_{-1} = \frac{1}{a'\Delta_1} \left\{ \frac{1}{\chi_2}\frac{\partial C_{0,0}}{\partial q} - \frac{C_{0,0}}{\chi_2^2}\frac{\partial\chi_2}{\partial q} \right\} \sin\,\varpi\,\frac{\partial\theta_0}{\partial\tau},$$

the coefficient of μ in the right member of the equation for $\dfrac{d\delta\Omega}{dt}$ is equal to:

$$\frac{e'}{a'\Delta_1}\,v_1 \left\{ \frac{1}{\chi_2}\frac{\partial C_{0,0}}{\partial q} - \frac{C_{0,0}}{\chi_2^2}\frac{\partial\chi_2}{\partial q} \right\} \frac{\partial^2\Omega_1}{\partial\tau^2}\,\sin\,\varpi.$$ (25)

The resulting development for $\delta\Omega$ is:

$$\delta\Omega = e' \sum_{p=0}^{p=\infty} \Omega^{(e')}_p \mu^p,$$

$$\Omega^{(e')}_p = \sum_{-\infty}^{+\infty} \Omega^{(p,q)}_{(e')} \sin\,(\varpi + q\tau).$$

(26)

6. For the determination of the coefficients $I_{p,0}, .., V_{p,0}, II_{p,-1}, V_{p,-1}$ the following formulae result from (13):

$$\sum_{-\infty}^{+\infty} I_{p,0} \sin(\varpi + p\tau) =$$
$$= -\frac{e'}{a'\Delta_1 v_1} \frac{\partial \theta_0}{\partial q} \sum_{p=1}^{p=\infty} [C_{p,0} \cos(\varpi + p\tau) + C_{-p,0} \cos(\varpi - p\tau)], \qquad (27)$$

$$\sum_{-\infty}^{+\infty} II_{v,0} \sin(\varpi + p\tau) = \frac{e'}{a'\Delta_1 \chi_2} \frac{\partial C_{0,0}}{\partial q} \sin \varpi \frac{\partial \theta_1}{\partial \tau} +$$
$$+ \frac{e'}{a'\Delta_1 v_1} \frac{\partial \theta_0}{\partial \tau} \sum_{p=1}^{p=\infty} \left[\frac{\partial C_{p,0}}{\partial q} \frac{\sin(\varpi + p\tau)}{p} - \frac{\partial C_{-p,0}}{\partial q} \frac{\sin(\varpi - p\tau)}{p} \right], \qquad (28)$$

$$\sum_{-\infty}^{+\infty} III_{p,0} \sin(\varpi + p\tau) = \frac{e'}{a'\Delta_1 \chi_2} C_{0,0} \left[\frac{\partial \Omega_1}{\partial \tau} \frac{\partial \theta_0}{\partial q} - \frac{\partial \Omega_1}{\partial q} \frac{\partial \theta_0}{\partial \tau} \right] \cos \varpi, \qquad (29)$$

$$\sum_{-\infty}^{+\infty} IV_{p,0} \sin(\varpi + p\tau) =$$
$$= -\frac{e'}{a'\Delta_1 v_1^2} \frac{\partial v_1}{\partial q} \frac{\partial \theta_0}{\partial \tau} \sum_{p=1}^{p=\infty} \left[C_{p,0} \frac{\sin(\varpi + p\tau)}{p} - C_{-p,0} \frac{\sin(\varpi - p\tau)}{p} \right], \qquad (30)$$

$$\sum_{-\infty}^{+\infty} V_{p,0} \sin(\varpi + p\tau) = -\frac{e'}{a'\Delta_1} \frac{C_{0,0}}{\chi_2^2} \frac{\partial \chi_2}{\partial q} \sin \varpi \frac{\partial \theta_1}{\partial \tau}, \qquad (31)$$

$$\sum_{-\infty}^{+\infty} II_{p,-1} \sin(\varpi + p\tau) = \frac{e'}{a'\Delta_1 \chi_2} \frac{\partial C_{0,0}}{\partial q} \sin \varpi \frac{\partial \theta_0}{\partial \tau}, \qquad (32)$$

$$\sum_{-\infty}^{+\infty} V_{p,-1} \sin(\varpi + p\tau) = -\frac{e'}{a'\Delta_1} C_{0,0} \frac{1}{\chi_2^2} \frac{\partial \chi_2}{\partial q} \sin \varpi \frac{\partial \theta_0}{\partial \tau}. \qquad (33)$$

In taking the derivatives in the right members of these formulae the corresponding quantitities are to be considered as functions of ϱ_0, σ_0, q and τ.

The values of $I_{p,0}, .., V_{p,0}, \theta_{(e')}^{(0,p)}$ resulting from (27)—(31) and (20) have been collected in the first table of the next page.

The coefficients $\theta_{(e')}^{(-1,q)}$ result from the equation

$$\sum_{-\infty}^{+\infty} \theta_{(e')}^{(-1,q)} \sin(\varpi + q\tau) = \frac{1}{a'\Delta_1 \chi_2} \left\{ \frac{\partial C_{0,0}}{\partial q} - \frac{C_{0,0}}{\chi_2} \frac{\partial \chi_2}{\partial q} \right\} \sin \varpi \frac{\partial \theta_0}{\partial \tau}; \qquad (34)$$

here, in taking the derivatives, ϱ_0 is to be considered constant.
Hence:

$$\theta_{(e')}^{(-1,2q)} = 0, \qquad q = 0, \pm 1, \pm 2, ... \qquad (35)$$

The values of the coefficients with odd index have been collected in the second table of the next page.

p	$I_{p,0}\dfrac{10^4}{e'}$	$II_{p,0}\dfrac{10^4}{e'}$	$III_{p,0}\dfrac{10^4}{e'}$	$IV_{p,0}\dfrac{10^4}{e'}$	$V_{p,0}\dfrac{10^4}{e'}$	$\theta_{(e)}^{(0,p)}\cdot 10^4$
− 6	− 5	+ 6	0	0	0	+ 1
− 5	− 12	+ 13	+ 3	0	0	+ 4
− 4	+ 370	− 381	0	+ 7	0	− 4
− 3	+ 339	− 359	+ 12	+ 6	0	− 2
− 2	− 19696	+ 20464	0	− 739	− 23	+ 6
− 1	− 331	− 371	+ 466	+ 6	0	− 230
0	+ 38663	+ 41633	0	− 1493	0	+ 78803
+ 1	+ 331	+ 371	− 466	− 6	0	+ 230
+ 2	− 19696	+ 20464	0	− 739	− 23	+ 6
+ 3	− 339	+ 359	− 12	− 6	0	+ 2
+ 4	+ 370	− 381	0	+ 7	0	− 4
+ 5	+ 12	− 13	− 3	0	0	− 4
+ 6	− 5	+ 6	0	0	0	+ 1

q	$\theta_{(e')}^{(-1,q)}\cdot 10^5$
− 3	− 4
− 1	+ 770
+ 1	+ 770
+ 3	− 4

For the determination of $\sigma_0^{(e')}$ we have:

$$\sigma_0^{(e')} = \frac{C_{0,0}}{a'\chi_2}\cos \varpi, \tag{36}$$

hence:

$$\sigma_{(e')}^{(0,q)} = 0 \quad \text{if} \quad q \neq 0 \quad ; \quad \sigma_{(e')}^{(0,0)} = -\,0.090563\,\sqrt{a_\bullet M} \ . \tag{37}$$

For $\varrho_0^{(e')}$ we have:

$$\varrho_0^{(e')} = -\,\frac{v_1}{\left[\dfrac{\partial^2 R_0}{\partial \varrho^2}\right]_{\rho_0}}\cdot \frac{\partial \theta_{-1}^{(e')}}{\partial \tau}. \tag{38}$$

The resulting values of $\varrho_{(e')}^{(0,q)}$ have been collected in the next table.

q	$\varrho_{(e')}^{(0,q)} \dfrac{10^4}{\varrho_0}$
-1	$+13$
$+1$	-13

From the expression for $\Omega_0^{(e')}$, viz.

$$\Omega_0^{(e')} = [\ldots] \sin \varpi + 0.024 \frac{\partial \Omega_1}{\partial r} \sin \varpi, \tag{39}$$

we deduce:

$$\Omega_{(e')}^{(0,2q+1)} = 0, \qquad q = 0, \pm 1, \pm 2, \ldots, \tag{40}$$

and further the values of the next table.

q	$\Omega_{(e')}^{(0,q)} \cdot 10^4$
-2	-3
0	$[\ldots]$
$+2$	-3

The development of the perturbative function has not been carried on far enough to enable us to compute the quantity $[\ldots]$.

7. Passing from the terms of the first order with respect to e' of ϱ and σ to the corresponding terms of a and e, viz. δa and δe, we have:

$$\frac{\delta a}{a_0} = \frac{\partial a}{\partial \varrho} \frac{\delta \varrho}{a_0} = \frac{2\varrho}{\varrho_0} \frac{\delta \varrho}{\varrho_0}, \tag{41}$$

$$\dot{\delta e} = \frac{\sqrt{1-e^2}}{e} (\sqrt{1-e^2} - \tfrac{3}{4}) \frac{\delta \varrho}{\varrho} - \frac{\sqrt{1-e^2}}{e} \frac{\delta \sigma}{\sqrt{aM}}. \tag{42}$$

Denoting the terms of the first order with respect to e' of the variables l and g by δl and δg, we have [1]):

$$\delta \theta = 4 \delta l + 3 \delta g,$$
$$\delta \Omega = \delta g;$$

hence:

$$\delta l = \frac{\delta \theta - 3 \delta \Omega}{4}, \tag{43}$$
$$\delta g = \delta \Omega$$

The following tables contain the developments of the four quantities $\delta a, \delta e, \delta l, \delta g$ and numerical values of the coefficients.

[1]) Investigations, Chapter II, § 2.

$$dl = e' \sum_{p=0''}^{p=\infty} l_p^{(e')} \mu^p + e' l_{-1}^{(e')} \mu^{-1} \qquad l_p^{(e')} = \sum_{-\infty}^{+\infty} l_{(e')}^{(p,q)} \sin(\varpi + q\tau), \; p = -1, 0, \ldots$$

$$
l_{-1}^{(e')} =
\begin{array}{l}
- \overset{\circ}{0}.001 \; sin \, (\varpi - 3\tau) \\
+ 0.110 \; sin \, (\varpi - \tau) \\
+ 0.110 \; sin \, (\varpi + \tau) \\
- 0.001 \; sin \, (\varpi + 3\tau)
\end{array}
$$

$$
l_0^{(e')} =
\begin{array}{l}
+ \overset{\circ}{0}.02 \; sin \, (\varpi - 2\tau) \\
- 0.33 \; sin \, (\varpi - \tau) \\
\left[\ldots\ldots\right] \; sin \, \varpi \\
0.33 \; sin \, (\varpi + \tau) \\
+ 0.02 \; sin \, (\varpi + 2\,\tau)
\end{array}
$$

$$l_{(e)}^{(-1,2q)} = 0, \quad q = 0, \pm 1, \pm 2, \ldots$$

$$dg = e' \sum_{p=0}^{p=\infty} g_p^{(e')} \mu^p$$

$$g_p^{(e')} = \sum_{-\infty}^{+\infty} g_{(e')}^{(p,q)} \sin(\varpi + q\tau)$$

$$
g_0^{(e')} =
\begin{array}{l}
- \overset{\circ}{0}.02 \; sin \, (\varpi - 2\tau) \\
\left[\ldots\ldots\right] \; sin \, \varpi \\
- 0.02 \; sin \, (\varpi + 2\tau)
\end{array}
$$

$$g_{(e')}^{(0,2q+1)} = 0, \quad q = 0, \pm 1, \pm 2, \ldots$$

$$da = e' \sum_{p=0}^{p=\infty} a_p^{(e')} \mu^p \qquad\qquad de = e' \sum_{p=0}^{p=\infty} e_p^{(e')} \mu^p$$

$$a_p^{(e')} = \sum_{-\infty}^{+\infty} a_{(e')}^{(p,q)} \cos(\varpi + q\tau) \qquad e_p^{(e')} = \sum_{-\infty}^{+\infty} e_{(e')}^{(p,q)} \cos(\varpi + q\tau)$$

$$
\frac{a_0^{(e')}}{a_0} =
\begin{array}{l}
+ 0.0026 \; cos \, (\varpi - \tau) \\
- 0.0026 \; cos \, (\varpi + \tau)
\end{array}
$$

$$
e_0^{(e')} =
\begin{array}{l}
+ 0.0030 \; cos \, (\varpi - \tau) \\
+ 0.8636 \; cos \, \varpi \\
- 0.0030 \; cos \, (\varpi + \tau)
\end{array}
$$

$$a_{(e')}^{(0,2q)} = 0, \quad q = 0, \pm 1, \pm 2, \ldots$$

8. For the numerical computation of the perturbations $\delta a, \delta e, \delta l, \delta g$ we take [1])

$$e' = 0.02870.$$

From the period of libration we deduced [2]):

$$\frac{1}{\mu^2} = 3986;$$

from the motion of the pericentre [3]):

$$\frac{1}{\mu^2} = 4080.$$

Taking the mean of these values, we get:

$$\frac{1}{\mu^2} = 4033,$$

hence:

$$\mu = 0.0157.$$

Neglecting terms of the order one and higher in μ of the developments of $\delta l, \delta g, \delta a, \delta e$, which have been given at the head of each table of the preceding section, we get for $\delta l, \delta g, \delta a, \delta e$ the values collected in the following table.

$\delta l =$	$\delta g =$	$\dfrac{\delta a}{a_0} =$	$\delta e =$
$-\overset{o}{0.002}\ sin\,(\varpi - 3\tau)$			
$+\,0.001\ sin\,(\varpi - 2\tau)$	$-\,0.001\ sin\,(\varpi - 2\tau)$		
$+\,0.192\ sin\,(\varpi - \tau)$		$+\,0.0001\ cos\,(\varpi - \tau)$	$+\,0.0001\ cos\,(\varpi - \tau)$
$[\ldots]\ sin\ \varpi$	$[.\ ..]\ sin\ \varpi$		$+\,0.0248\ cos\ \varpi$
$+\,0.211\ sin\,(\varpi + \tau)$		$-\,0.0001\ cos\,(\varpi + \tau)$	$-\,0.0001\ cos\,(\varpi + \tau)$
$+\,0.001\ sin\,(\varpi + 2\tau)$	$-\,0.001\ sin\,(\varpi + 2\tau)$		
$-\,0.002\ sin\,(\varpi + 3\tau)$			

The agreement of the coefficient of $cos\,\varpi$ in δe with the value derived from observation by H. STRUVE [4]), viz. $+\ 0.0230$, is very satisfactory.

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[1]) Investigations, p. 71.
[2]) l. c., p. 70.
[3]) Proceedings, Vol. XXI, N⁰. 6 and 7.
[4]) Publications de l'Observatoire Central Nicolas. Série II. Vol. XI. Beobachtungen der Saturnstrabanten. St. Pétersbourg, 1898, p. 290.

Physics. — *"On the connexion between geometry and mechanics in static problems".* By Prof. J. A. SCHOUTEN and D. J. STRUIK. (Communicated by Prof. H. A. LORENTZ).

Connexions between the geodetic differentiations belonging to different fundamental tensors.

When in a space two different fundamental tensors $^2\mathbf{l}$ and $^2\mathbf{j}$ are given [1]), we have the following general theorem:

The geodetic differential quotient of a given affinor with respect to $^2\mathbf{j}$ is equal to the sum of the geodetic differential quotient with respect to $^2\mathbf{l}$ and the product of the affinor by a simultaneous covariant of $^2\mathbf{j}$ and $^2\mathbf{l}$. The same holds for the geodetic differentials.

Let us first give the proof for a vector. When

$$\left. \begin{array}{ll} ^2\mathbf{l} = \mathbf{a}^2 = \mathbf{a}_1{}^2 = \ldots & ^2\mathbf{j} = \mathbf{z}^2 = \mathbf{z}_1{}^2 = \ldots \\ ^2\mathbf{l'} = \mathbf{a'}^2 = \mathbf{a'}_1{}^2 = \ldots & ^2\mathbf{j'} = \mathbf{z'}^2 = \mathbf{z'}_1{}^2 = . \end{array} \right\} \quad \cdots \quad (1)$$

then we have:

$$\left. \begin{array}{ll} \mathbf{a'} = {}^2\mathbf{l'} \mathbin{\underset{.}{|}} \mathbf{a} & \mathbf{z'} = {}^2\mathbf{j'} \mathbin{\underset{.}{|}} \mathbf{z} \\ \mathbf{a} = {}^2\mathbf{l} \mathbin{\underset{.}{|}} \mathbf{a'} & \mathbf{z} = {}^2\mathbf{j} \mathbin{\underset{.}{|}} \mathbf{z'} \end{array} \right\} \quad \cdots \cdots \quad (2)$$

$$\mathbf{aa'} = \mathbf{zz'} = \sum_\lambda \mathbf{e}_\lambda \mathbf{e}_\lambda{}' \,) \quad \cdots \cdots \quad (3)$$

When ∇ and d are the symbols of the geodetic differentiation belonging to $^2\mathbf{l}$ and $'\nabla$ and $'d$ those belonging to $^2\mathbf{j}$, then we have the following relations for an arbitrary scalar p and for an arbitrary vector $\mathbf{v}$ resp. $\mathbf{v'}$:

$$'\nabla p = \nabla p \quad \cdots \cdots \cdots \quad (4)$$

$$\begin{array}{l} '\nabla\mathbf{v} = {}'\nabla(\mathbf{z'}\mathbin{\underset{.}{|}}\mathbf{v})\mathbf{z} = \nabla(\mathbf{z'}\mathbin{\underset{.}{|}}\mathbf{v})\mathbf{z} = \nabla\mathbf{v} + \mathbf{v}\mathbin{\underset{.}{|}}\mathbf{a'}\nabla(\mathbf{a}\mathbin{\underset{.}{|}}\mathbf{z})\mathbf{z} = \nabla\mathbf{v} - \mathbf{v}\mathbin{\underset{.}{|}}\mathbf{z'}\nabla(\mathbf{z}\mathbin{\underset{.}{|}}\mathbf{a'})\mathbf{a} \\ '\nabla\mathbf{v'} = {}'\nabla(\mathbf{z}\mathbin{\underset{.}{|}}\mathbf{v'})\mathbf{z'} = \nabla(\mathbf{z}\mathbin{\underset{.}{|}}\mathbf{v'})\mathbf{z'} = \nabla\mathbf{v'} + \mathbf{v'}\mathbin{\underset{.}{|}}\mathbf{a}\nabla(\mathbf{a'}\mathbin{\underset{.}{|}}\mathbf{z})\mathbf{z'} = \nabla\mathbf{v'} - \mathbf{v'}\mathbin{\underset{.}{|}}\mathbf{z}\nabla(\mathbf{z'}\mathbin{\underset{.}{|}}\mathbf{a})\mathbf{a'} \,) \end{array} \quad (5)$$

or when we introduce the notation [4]):

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[1]) For the notations used in this paper we refer to: J. A. SCHOUTEN, Die Analysis zur neueren Relativitätstheorie, Verh. der Kon. Akad. v. Wet. Dl. XII. N⁰. 6. cited further on as A. R.

[2]) As we shall have to do with different fundamental tensors, we must distinguish between covariant and contravariant quantities while else this is not necessary. Between two quantities **p** and **p'** no relation exists, unless this has been stated especially.

[3]) Comp. A. R. p. 44.

[4]) Comp. A. R. p. 89, formula (101).

$$\overset{3..,}{\mathbf{A}} = \mathbf{a}\nabla(\mathbf{z}! \; \mathbf{a'})\mathbf{z'} = -\mathbf{z}\nabla(\mathbf{a}! \; \mathbf{z'})\mathbf{a'} = \mathbf{a}\;\nabla\mathbf{a'} - \mathbf{z}\nabla\mathbf{z'}\;^1) \quad . \quad . \quad (6)$$

or shorter:

$$\left. \begin{aligned} '\nabla\mathbf{v} &= \nabla\mathbf{v} - \overset{3..,}{\mathbf{A}} \overset{1}{.} \mathbf{v} \\ '\nabla\mathbf{v'} &= \nabla\mathbf{v'} + \mathbf{v'}! \; \overset{3..,}{\mathbf{A}} \end{aligned} \right\} \;^2) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The affinor $\overset{3..,}{\mathbf{A}}$ is a simultaneous covariant of $^2\mathbf{l}$ and $^2\mathbf{j}$, symmetrical with respect to the two first ideal factors, $\nabla \times \mathbf{v} = {'\nabla} \times \mathbf{v}$ being independent of the fundamental tensor ^{3}). In the same way we have:

$$'dp = dp \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$\left. \begin{aligned} 'd\mathbf{v} &= d\mathbf{v} - d\mathbf{x'}! \; \overset{3..,}{\mathbf{A}} \overset{1}{.} \mathbf{v} \\ 'd\mathbf{v'} &= d\mathbf{v'} + d\mathbf{x'v'}! \; \overset{3..,}{\mathbf{A}} \end{aligned} \right\} \;^4) \quad . \quad . \quad . \quad . \quad (9)$$

For every covariant affinor $\overset{p}{\mathbf{v}} = \mathbf{v}_1 \ldots \mathbf{v}_p$ we find, taking into consideration:

$$\overset{p}{\mathbf{v}} = (\mathbf{a'}! \; \mathbf{v}_i)\; \mathbf{v}_1 \ldots \mathbf{v}_{i-1} \, \mathbf{a} \, \mathbf{v}_{i+1} \ldots \mathbf{v}_p \;^5) \quad . \quad . \quad . \quad (10)$$

and the equation:

$$\overset{p}{\mathbf{v}} = \mathbf{a}_1 \ldots \mathbf{a}_p \, (\mathbf{a}_1'.\mathbf{v}_1) \ldots (\mathbf{a}_p'.\mathbf{v}_p) = \mathbf{a}_1 \ldots \mathbf{a}_p \, \mathbf{a}_p' \ldots \mathbf{a}_1' \; \overset{p}{.} \; \overset{p}{\mathbf{v}} \quad . \quad (10a)$$

which follows from (10) and making use of (7):

$$\left. \begin{aligned} '\overset{p}{\nabla\mathbf{v}} &= \overset{1,..p}{\underset{i}{\Sigma}} ('\nabla\mathbf{v}_i)! \; \mathbf{a'v}_1 \ldots \mathbf{v}_{i-1} \, \mathbf{a} \, \mathbf{v}_{i+1} \ldots \mathbf{v}_p = \\ &= \nabla\overset{p}{\mathbf{v}} - \overset{1,..p}{\underset{i}{\Sigma}} (\overset{3..,}{\mathbf{A}} \overset{1}{.} \mathbf{v}_i)\; \mathbf{a'} \, \mathbf{v}_1 \ldots \mathbf{v}_{i-1} \, \mathbf{a} \mathbf{v}_{i+1} \ldots \mathbf{v}_p = \\ &= \nabla\overset{p}{\mathbf{v}} - \left\{ \overset{1,..p}{\underset{i}{\Sigma}} (\overset{3..,}{\mathbf{A}} \overset{1}{.} \mathbf{a}_i)! \; \mathbf{a'} \, \mathbf{a}_1 \ldots \mathbf{a}_{i-1} \, \mathbf{a} \, \mathbf{a}_{i+1} \ldots \mathbf{a}_p \, \mathbf{a}_p' \ldots \mathbf{a}_1' \right\} \overset{p}{.} \overset{p}{\mathbf{v}}, \end{aligned} \right\} \quad (11)$$

and therefore:

$$'d\overset{p}{\mathbf{v}} = d\overset{p}{\mathbf{v}} - d\mathbf{x'}! \left\{ \overset{1,..p}{\underset{i}{\Sigma}} (\overset{3..,}{\mathbf{A}} \overset{1}{.} \mathbf{a}_i)! \; \mathbf{a'} \, \mathbf{a}_1 \ldots \mathbf{a}_{i-1} \, \mathbf{a} \, \mathbf{a}_{i+1} \ldots \mathbf{a}_p \, \mathbf{a}_p' \ldots \mathbf{a}_1' \right\} \overset{p}{.} \overset{p}{\mathbf{v}}. \quad (12)$$

This is the proof for a covariant affinor. For contravariant and mixed affinors the proof can be given in the same way.

For the special case that:

$$^2\mathbf{l} = \underset{j}{\Sigma} \, \mathbf{e}_\lambda \mathbf{e}_\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

---

^{1}) A mixed affinor will be indicated by an index of points and commas referring to the place of the covariant and contravariant ideal vectors.

^{2}) Comp. A. R. p. 89 form. (103b).

^{3}) Comp. A. R. p. 55.

^{4}) Comp. A. R. p. 89 form. (103a).

^{5}) Comp. A. R. p. 54 form. (74).

the equations between the characteristic numbers become the well-known relations between the geodetic differentiation and the ordinary partial derivations with respect to the fundamental variables x^i. For this case the characteristic numbers of $\overset{3..,}{\mathbf{A}}$ become the Christoffel-symbols $\left\{ \begin{matrix} \lambda\mu \\ \nu \end{matrix} \right\}$.

We shall apply the proved theorem to a static problem of the theory of relativity.

Space and time in static problems.

In the theory of relativity in general we cannot speak of "the" space. Only in thus-called static problems in which the line-element has the form:

$$ds^2 = g_{aa}\, dx^a + \overset{b,c,d}{\underset{i,j}{\sum}} g_{i\mu}\, dx^i\, dx^\mu = g_{aa}\, dx^a - dl^2 \quad . \quad . \quad . \quad (14)$$

where g_{aa} and $g_{i\mu}$ depend on x^b, x^c and x^d *only*, we can ascribe a definite meaning to the words space and time, at least when dx^a is considered as a differential of the time, dt, and dl as a line-element of the space and when *always* the problem is treated statically.

The motion of a material point in a static gravitation field.

The equations of motion of a material point (which is supposed not to alter the field) are:

$$\delta \int ds = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

This equation can be transformed into:

$$\delta \int \sqrt{g_{aa}\, dt^2 - dl^2} = \delta \int_{t_2}^{t_1} \sqrt{g_{aa} - \left(\frac{dl}{dt}\right)^2}\, dt = 0 \quad . \quad . \quad (16)$$

When now g_{aa} has the form $(1-\varepsilon)c^2$, where ε is very small and when $\left(\frac{dl}{dt}\right)^2$ is of the order of magnitude of εc^2, we have, neglecting quantities of the order ε^2:

$$\delta \int ds = \delta \int_{t_2}^{t_1} \left(1 - \frac{\varepsilon}{2}\right)c^2 - \frac{1}{2}\left(\frac{dl}{dt}\right)^2\, dt = -\delta \int_{t_2}^{t_1} \left\{\frac{\varepsilon}{2}c^2 + \frac{1}{2}\left(\frac{dl}{dt}\right)^2\right\}\, dt = 0. (17)$$

Equations of motion of non-euclidian classic mechanics.

By "classic" mechanics in a space with the line-element dl we shall understand mechanics with the fundamental equation:

$$^2\mathrm{l'}\!\mathrm{1}\; \mathbf{K} = m\,\frac{d}{dt}\frac{d\mathbf{x'}}{dt}\;\;^1) \qquad \ldots \ldots \quad (18)$$

where 'l' is written for the contravariant fundamental tensor, $\mathbf{K}$ for the force and $d\mathbf{x'}$ for the line-element and where the second differentiation is of course a geodetic one. As because of (18):

$$^2\mathrm{l'}\!\mathrm{1}\; \mathbf{K} = m\,\frac{d^2l}{dt^2}\frac{d\mathbf{x'}}{dl} + m\left(\frac{dl}{dt}\right)^2\frac{d}{dl}\frac{d\mathbf{x'}}{dl}, \qquad \ldots \quad (19)$$

a free point moves in such mechanics along a geodetic line:

$$\frac{d}{dl}\frac{d\mathbf{x'}}{dl} = 0 \;. \qquad \ldots \ldots \ldots \quad (20)$$

When $\dfrac{\mathbf{K}}{m}$ is the gradient of a force-function U we have for such mechanics the variation theorem:

$$\delta\!\int_{t_2}^{t_1} \left\{ U + \tfrac{1}{2}\left(\frac{dl}{dt}\right)^2 \right\} dt = 0 \;, \qquad \ldots \ldots \quad (21)$$

for:

$$\delta\!\int_{t_2}^{t_1}\left\{ U + \tfrac{1}{2}\left(\frac{dl}{dt}\right)^2 \right\}dt = \delta\!\int_{t_2}^{t_1}\left(U + \tfrac{1}{2}\,^2\mathrm{l}\mathrm{2}\,\frac{d\mathbf{x'}}{dt}\frac{d\mathbf{x'}}{dt} \right)dt =$$

$$= \int_{t_2}^{t_1}\left\{ \delta\mathbf{x'}\!\mathrm{1}\;\nabla U + {}^2\mathrm{l}\mathrm{2}\left(\frac{d\mathbf{x'}}{dt}\,\delta\frac{d\mathbf{x'}}{dt}\right) \right\}dt = \int_{t_2}^{t_1}\left\{ \delta\mathbf{x'}\mathrm{1}\;\nabla U + {}^2\mathrm{l}\mathrm{2}\left(\frac{d\mathbf{x'}}{dt}\,d\frac{\delta\mathbf{x'}}{dt}\right) \right\}dt\;^2) = \quad (22)$$

$$= \Big/\,_{t_2}\; {}^2\mathrm{l}\mathrm{2}\left(\frac{d\mathbf{x'}}{dt}\,\delta\mathbf{x'}\right) + \int_{t_2}^{t_1}\delta\mathbf{x'}\!\mathrm{1}\;\left\{ \nabla U - {}^2\mathrm{l}\mathrm{1}\,\frac{d}{dt}\frac{d\mathbf{x'}}{dt} \right\}dt, \;\ldots \ldots$$

and according to (18) we have now:

$$^2\mathrm{l'}\!\mathrm{1}\;\nabla U = \frac{d}{dt}\frac{d\mathbf{x'}}{dt}. \qquad \ldots \ldots \ldots \quad (23)$$

---

¹) A force being a covariant vector and an acceleration a contravariant one, a force and an acceleration become quantities of a different kind, as soon as the two kinds may no longer be identified In that case the mass becomes a quantity with the mode of orientation of the covariant fundamental tensor.

²) Because we have for the geodetic differentiations d and δ, $\delta d\mathbf{x'} = d\delta\mathbf{x'}$, see A.R. p. 57 form. (103).

Reduction of the four-dimensional problem to a three-dimensional one.

Comparing (17) and (21) we see, that the motion of a material point can be considered as a motion according to classic mechanics in a space with a line-element dl and a force-function:

$$U = \frac{\varepsilon}{2} c^2. \qquad \qquad \qquad \text{[1]) (24)}$$

Using the line-element calculated by SCHWARZSCHILD:

$$
\left.
\begin{aligned}
ds^2 &= c^2 \left(1 - \frac{a}{r}\right) dt^2 - dl^2 \\[2mm]
dl^2 &= \left(1 + \frac{a}{r}\right) dr^2 + r^2 \sin^2\theta\, d\varphi^2 + r^2 d\theta^2
\end{aligned}
\right\} \quad \ldots \quad (25)
$$

for the gravitation field of a single centre, we find

$$U = \frac{ac^2}{2r} = \varkappa^2 \frac{M_0}{r} \quad , \quad \ldots \ldots \quad (26)$$

where $\varkappa$ represents the gravitation constant and M_0 the mass of the centre, while the reduction holds for velocities of the order of magnitude of $\frac{a}{r} c$, when quantities of the order $\frac{a^2}{r^2}$ are neglected. Therefore equations (18) can give us the motion, and thus also e.g. the perihelium motion of Mercurius just as well as equations (15). In this connexion we may therefore say, that the perihelium motion is "due" to the being non euclidian of the space in the neighbourhood of the sun and this gives an "explanation" of the phenomenon from the point of view of classic though non-euclidian mechanics.

Passage to another line-element.

Besides the fundamental tensors:

$$
\left.
\begin{aligned}
^2\mathbf{1} = \mathbf{a}^2 = \mathbf{a}_1{}^2 = \ldots &= \left(1 + \frac{a}{r}\right) \mathbf{e}_r\, \mathbf{e}_r + r^2 \sin^2\theta\, \mathbf{e}_\varphi\, \mathbf{e}_\varphi + r^2\, \mathbf{e}_\theta\, \mathbf{e}_\theta \\[2mm]
^2\mathbf{1}' = \mathbf{a}'^2 = \mathbf{a}_1{}'^2 = \ldots &= \left(1 - \frac{a}{r}\right) \mathbf{e}'_r\, \mathbf{e}'_r + \frac{1}{r^2 \sin^2\theta}\, \mathbf{e}'_\varphi\, \mathbf{e}'_\varphi + \frac{1}{r^2}\, \mathbf{e}'_\theta\, \mathbf{e}'_\theta
\end{aligned}
\right\} \quad \ldots \quad (27)
$$

with the relations:

$$\mathbf{a} = {}^2\mathbf{1}! \ \mathbf{a}' \quad , \quad \mathbf{a}' = {}^2\mathbf{1}'! \ \mathbf{a} \quad , \quad {}^2\mathbf{1}! \ {}^2\mathbf{1}' = \overset{r,\varphi,\theta}{\underset{\lambda}{\Sigma}} \mathbf{e}_\lambda\, \mathbf{e}'_\lambda , \quad \ldots \quad (28)$$

---

[1]) In his paper Statica Einsteiniana, Rend. dei Lincei 21 (17) 449—470, T. LEVI CIVITA has shown that without neglection of quantities of the order ε^2 the four-dimensional problem can be reduced to a three dimensional one. A new auxiliary variable t^* however is used then as "time". A. PALATINI has applied this to the line-element of SCHWARZSCHILD and the perihelium motion: Lo spostamento del perielio di mercurio etc, Nuovo Cimento 14 (17) 12—54.

we introduce the fundamental tensors :

$$^2\mathbf{j} = \mathbf{z}^2 = \mathbf{z}_1{}^2 = \ldots = \mathbf{e}_r\,\mathbf{e}_r + r^2\sin^2\theta\,\mathbf{e}_\varphi\,\mathbf{e}_\varphi + r^2\,\mathbf{e}_\theta\,\mathbf{e}_\theta$$

$$^2\mathbf{j}' = \mathbf{z}'^2 = \mathbf{z}'_1{}^2 = \ldots = \mathbf{e}'_r\,\mathbf{e}'_r + \frac{1}{r^2\sin^2\theta}\,\mathbf{e}'_\varphi\,\mathbf{e}'_\varphi + \frac{1}{r^2}\,\mathbf{e}'_\theta\,\mathbf{e}'_\theta \qquad (29)$$

with the relations :

$$\mathbf{z} = {}^2\mathbf{j}\,!\,\mathbf{z}'\quad,\quad \mathbf{z}' = {}^2\mathbf{j}'\,!\,\mathbf{z}\quad,\quad {}^2\mathbf{j}\,!\,{}^2\mathbf{j}' = {}^2\mathbf{1}\,!\,{}^2\mathbf{1}' \quad . \quad . \quad . \quad (30)$$

Evidently the fundamental tensors $^2\mathbf{j}$ and $^2\mathbf{j}'$ give a euclidian line-element.

For the indicated values $^2\mathbf{1}$ and $^2\mathbf{j}$ we then have :

$$\mathbf{A} \overset{3..}{=} \Sigma(z_{\lambda\mu}\,z^\nu - a_{\lambda\mu}a^\nu)\,\mathbf{e}_\lambda\mathbf{e}_\mu\mathbf{e}'_\nu =$$

$$= -\tfrac{1}{2}\frac{a}{r^2}\Big(1 - \frac{a}{r}\Big)\mathbf{e}_r\mathbf{e}_r\mathbf{e}'_r - r\Big(1 - \frac{a}{r}\Big)\mathbf{e}_\theta\mathbf{e}_\theta\mathbf{e}'_r + r\,\mathbf{e}_\theta\mathbf{e}_\theta\mathbf{e}'_r -$$

$$- r\sin^2\theta\Big(1 - \frac{a}{r}\Big)\mathbf{e}_\varphi\mathbf{e}_\varphi\mathbf{e}'_r + r\sin^2\theta\,\mathbf{e}_\varphi\mathbf{e}_\varphi\mathbf{e}'_r - \qquad (31)$$

$$- \sin\theta\cos\theta\,\mathbf{e}_\varphi\mathbf{e}_\varphi\mathbf{e}'_\theta + \sin\theta\cos\theta\,\mathbf{e}_\varphi\mathbf{e}_\varphi\mathbf{e}'_\theta =$$

$$= -\tfrac{1}{2}\frac{a}{r^2}\Big(1 - \frac{a}{r}\Big)\mathbf{e}_r\,\mathbf{e}_r\,\mathbf{e}'_r + a\,\mathbf{e}_\theta\mathbf{e}_\theta\mathbf{e}'_r + a\sin^2\theta\,\mathbf{e}_\varphi\mathbf{e}_\varphi\mathbf{e}'_r$$

Equations of motion for the euclidian fundamental tensor $^2\mathbf{j}$.

Applying the relations (9) to the equations of motion :

$$^2\mathbf{1}'\,!\,\nabla\,U = \frac{d}{dt}\frac{d\mathbf{x}'}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

we obtain :

$$^2\mathbf{1}'\,!\,\nabla\,U = \frac{'d}{dt}\frac{d\mathbf{x}'}{dt} - \frac{d\mathbf{x}'}{dt}\frac{d\mathbf{x}'}{dt}\overset{3..}{2}\,\mathbf{A} \quad . \quad . \quad . \quad . \quad (33)$$

In classic mechanics the equations for $^2\mathbf{j}$ would be :

$$^2\mathbf{j}'\,!\,'\nabla\,U = \frac{'d}{dt}\frac{d\mathbf{x}'}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

and, as $'\nabla\,U = \nabla\,U$, the problem can therefore also be regarded as a problem of euclidian classic mechanics with an additional force :

$$\mathbf{K}_l = {}^2\mathbf{j}^1\left\{({}^2\mathbf{1}' - {}^2\mathbf{j}')\,!\,\nabla\,U + \frac{d\mathbf{x}'}{dt}\frac{d\mathbf{x}'}{dt}\overset{3..}{2}\,\mathbf{A}\right\} \quad . \quad . \quad . \quad . \quad (35)$$

per unit of mass.

As :

$$\nabla\,U = \frac{ac^2}{2}\,\nabla\frac{1}{r} = -\frac{ac^2}{2r^2}\,\mathbf{e}_r\,, \quad . \quad . \quad . \quad . \quad . \quad (36)$$

and $\mathbf{e}'_r$ has the same direction as $\mathbf{e}_r$, $\mathbf{K}_l$ has the direction of $\mathbf{e}_r$. From the equations :

$$^2\mathbf{j'}\underline{?} \; ('\nabla \, U + \mathbf{K}_l) = \frac{'d}{dt} \frac{d\mathbf{x'}}{dt} \quad . \quad . \quad . \quad . \quad . \quad (37)$$

we can deduce the motion just as well as from (18). In this connexion we may therefore say that the perihelium motion of Mercurius is "due" to the fact that the gravitation is only in first approximation proportional to the square of the distance and that a correction has to be added which is a function of the velocity and of two affinors $^2\mathbf{j}$ and $\mathbf{A}''$, definitely given in each point of the euclidian space. This gives another "explanation" of the phenomenon, from the point of view of classic euclidian mechanics with a correction force. When another arbitrary fundamental tensor is introduced instead of $^2\mathbf{j}$, another force has to be added. This gives again another "explanation", this time from the point of view of classic mechanics in a space with an arbitrary line element with a correcting force. It need hardly to be remarked that from the point of view of the theory of relativity all these "explanations", accurate to quantities of the order ε, are perfectly equivalent.

The remark first made by RIEMANN and accentuated so strongly later on among others by POINCARÉ, viz. that the question of the validity of a definite geometry is inseparable from the question of the validity of certain laws of nature, is evident for mechanics here. Equations (35) and (37) enable us to pass to new mechanics belonging to any new definition of measures.

Geodetic curvature of the path.

The equations of motion for $^2\mathbf{l}$ and $^2\mathbf{j}$ can be written in the following form:

$$\frac{1}{m}\,^2\mathbf{l'}\underline{?}\,\mathbf{K} = \frac{d^2l}{dt^2}\frac{d\mathbf{x'}}{dl} + \left(\frac{dl}{dt}\right)^2 \frac{d}{dl}\frac{d\mathbf{x'}}{dl} \quad . \quad . \quad . \quad . \quad (38)$$

$$\frac{1}{m}\,^2\mathbf{j'}\underline{?}\,(\mathbf{K}+m\mathbf{K}_l) = \frac{d^2j}{dt^2}\frac{d\mathbf{x'}}{dj} + \left(\frac{dj}{dt}\right)^2 \frac{'d}{dj}\frac{d\mathbf{x'}}{dj}, \quad . \quad . \quad (39)$$

where dl and dj represent the line-elements measured with $^2\mathbf{l}$ resp. $^2\mathbf{j}$. Therefore the curvature vector (viz. the vector perpendicular to the path which has a length equal to the geodetic curvature and a direction towards the side of the curvature [1]), is, measured in $^2\mathbf{l}$, equal to $\dfrac{d}{dl}\dfrac{d\mathbf{x'}}{dl}$ and to the component of $^2\mathbf{l'}\underline{?}\,\mathbf{K}$ perpendicular (measured

---

[1] When $\mathbf{i}_j$ determines a congruency, the curvature vector is $\mathbf{i}_j\,1\nabla\mathbf{i}_j$.

Comp. G. RICCI and T. LEVI CIVITA, Calcul différentiel absolu, Math. Ann. 54 (01) p. 154 or J. E. WRIGHT, Invariants of quadratic differential forms, Cambridge (08), p. 78.

in ^2l) to the path, divided by $m \left(\dfrac{dl}{dt}\right)^2$. Measured in $^2\mathbf{j}$ the curvature

vector $\dfrac{'d}{dj}\dfrac{d\mathbf{x}'}{dj}$ is equal to the component of $^2\mathbf{j}'$ ($\mathbf{K} + m\mathbf{K}_l$) perpendicular

(measured in $^2\mathbf{j}$) to the path, divided by $m \left(\dfrac{dj}{dt}\right)^2$. When the external

force is zero, (38) becomes:

$$0 = \frac{d^2l}{dt^2}\frac{d\mathbf{x}'}{dl} + \left(\frac{dl}{dt}\right)^2 \frac{d}{dl}\frac{d\mathbf{x}'}{dl} \quad \cdots \quad \cdots \quad (40)$$

or :

$$\frac{d^2l}{dt^2} = 0 \quad , \quad \frac{d}{dl}\frac{d\mathbf{x}'}{dl} = 0 . \quad \cdots \quad \cdots \quad (41)$$

and taking (35) into account, we find for (39):

$$0 = \frac{d^2j}{dt^2}\frac{d\mathbf{x}'}{dj} + \left(\frac{dj}{dt}\right)^2 \left\{ \frac{'d}{dj}\frac{d\mathbf{x}'}{dj} - \frac{d\mathbf{x}'}{dj}\frac{d\mathbf{x}'}{dj} \overset{3..,}{_2}\mathbf{A} \right\} \quad \cdots \quad (42)$$

Measured in ^2l the curvature vector is then equal to zero and

measured in $^2\mathbf{j}$ to the component of $\dfrac{d\mathbf{x}'}{dj}\dfrac{d\mathbf{x}'}{dj}\overset{3..,}{_2}\mathbf{A}$ perpendicular to

the path.

The change of geodetic curvature is perfectly given by the obtained equations.

When a vector $\mathbf{p}$ is moved geodetically once with respect to ^2l along $d\mathbf{x}'$ and another time with respect to $^2\mathbf{j}$, the directions of the two final positions will show a certain deviation from each other. We might be inclined to suppose this deviation per unit of length to be equal to the difference between the curvatures measured in the two different ways. The difference between $d\mathbf{p}$ and $'d\mathbf{p}$ is just equal to the difference between two vectors that first coincide with $\mathbf{p}$ and are then moved geodetically along $d\mathbf{x}'$ in two different ways. The problem however is not so simple, which is directly evident from the question whether the deviation and the unit of length have to be measured by ^2l or by $^2\mathbf{j}$. Measured by ^2l the curvature is:

$$\sqrt{\left(\frac{d}{dl}\frac{d\mathbf{x}'}{dl}\right)^2} \overset{2}{_2}{}^2l \quad \cdots \quad \cdots \quad (43)$$

and measured by $^2\mathbf{j}$:

$$\sqrt{\left(\frac{d}{dj}\frac{d\mathbf{x}'}{dj}\right)^2} \overset{2}{_2}{}^2\mathbf{j}. \quad \cdots \quad \cdots \quad (44)$$

and there is no simple relation between the difference of (43) and (44) and the mutual deviation measured in some way of the two possible geodetically moving systems of coordinates.

Physics. — *"On the Equation of State for Arbitrary Temperatures and Volumes. Analogy with* Planck's *Formula"*. By Dr. J. J. van Laar. (Communicated by Prof. H. A. Lorentz).

(Communicated in the meeting of January 25, 1919).

§ 1. Introduction.

In four papers[1] I tried more closely to study the dependence on the temperature of the quantities a and b of van der Waals's equation of state on the ground of *kinetic* considerations. I then came to the conclusion that the quantity a must steadily increase with descending temperature to a maximum value in the neighbourhood of the absolute zero point, after which it again decreases to the value 0 at $T = 0$. All this with very large volume.

Also with respect to b I carried out similar computations, but the mathematical difficulties become greater and greater, and the results obtained become very complicated. And for small volumes such a treatment of the problem is still less suitable. I, therefore, gave up the idea of publishing what was still found in connection with the said paper, and tried to solve the question by another and simpler way.

The thought had already occurred to me before, to substitute for the three-dimensional problem an analogous problem of one dimension, and then to transform the result in the well-known way to one which would hold for three dimensions. It is clear that so doing the *nature* of the sought dependence on the temperature and the volume of the constants occurring in the equation of state will not be modified; there can only arise some difference in a few *numerical* factors. But these are after all immaterial, when in the result some groups of quantities, the said factors included, are joined to one or more constants.

This method has besides also the advantage that it cannot only be used for large volumes, but also for *small volumes,* and results are, therefore, obtained which are universally valid, not only for arbitrary temperatures, but also for arbitrary *volumes,* from $v = \infty$ up to $v = b$.

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[1] These Proceedings XX, p. 750 and 1195; XXI, p. 2 and 16.

When calculating the different **time averages** — which up to now were too much neglected in this problem, the attention being almost exclusively concentrated on all kinds of spacial mean values, which can only modify some numerical values already alluded to above — it already soon appeared that the relation between the mean *Energy* and the *temperature* was the same for small volumes and low temperatures [1]) as the relation

$$E = E_0 + \frac{2E_0}{e^{\frac{^2/_3 E_0}{RT}} - 1} \quad ,$$

which was drawn up by PLANCK on behalf of the theory of radiation on assumption of the so-called hypothesis of quanta, in which only $^3/_2 Nhr$ would have to be substituted for E_0 to find back PLANCK's expression [2]).

By a *purely kinetic* way, on the sole foundation of the ordinary laws of *classical mechanics*, we could therefore derive PLANCK's famous expression, which I think was only possible up to now on the strength of very special suppositions, namely on the supposition that the energy is *emitted* only in entire multiples of the quantity hv ("energy quanta"). (The absorption can take place in arbitrary quantities according to the last modification applied by PLANCK in his theory).

§ 2. General Considerations on the Nature of the Attractive and Repulsive Forces.

We shall suppose the molecules to be all arranged along one dimension, and assume every arbitrary molecule M to move continually to and fro between the two adjacent molecules M_1 and M_2. Let the mean distance between the molecule centres be l (the analogon of the volume v for three dimensions), the radius of the sphere of attraction ϱ, the diameter of the molecule s. As M_1 and M_2 may
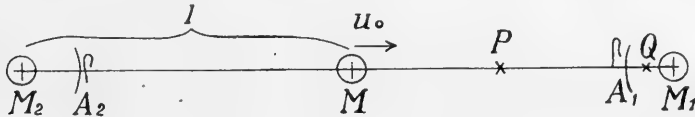
Fig. 1.

be found both on the lefthand side and on the righthand side of the mean places M_1 and M_2, we may suppose them to be on an average always in M_1 and M_2; besides we may assume M_1 and M_2

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[1]) With the difference only of a small finite term, which may be neglected by the side of the principal term, which becomes logarithmically infinite (see § 6).

[2]) I.e. multiplied by 3 on transition from a linear to a spacial oscillator.

to be at rest, because their movement may just as well be directed towards the left side as towards the right side (cf. however § 6). Hence M moves steadily to and fro between the molecules M_1 and M_2 assumed to be fixed. We call u_0 the velocity, which possesses M in the point in the middle between M_1 and M_2 (indicated by M in fig. 1: the so-called dead or neutral point), either to the lefthand side, or to the righthand side.

With this velocity M covers the part MA_1 (e.g. in P), but then it enters the sphere of attraction ϱ of the molecule M_1 (e.g. in Q); i.e. we assume that the attractive force does not make itself appreciably felt until the molecule has entered this sphere, and then increases steadily till M touches the molecule M_1 (distance of the middle points $= s$). Consequently the velocity u has also continually increased from A_1 to a maximum value u_s. Then repulsive forces appear; the two molecules are a little compressed and M is repelled. Between M_1 and M everything takes place in exactly the same way, only in opposite order; and between M and M_2 and back everything is again repeated. Hence we shall only have to consider the fourth part, viz. the portion MM_2 of every movement to and fro.

It is easily seen that three cases are possible. In the *first* place the case represented in fig. 1, in which $\overline{l > \varrho}$, and the molecule M, therefore, passes over a longer or shorter path *outside* the influence of the attraction of M_1, and *always* outside the sphere of attraction of M_2.

In the *second* place we have the transition case of fig. 2, viz. $\overline{l < \varrho}$, but $> \frac{1}{2} (\varrho + s)$. Then M is *continually within* the sphere of attraction $M_1 A_1$ of M_1, and besides during a period (from M to A_2, e.g. in P) also within that $(M_2 A_2)$ of M_2. As soon as M has passed the point A_2, e.g. in Q, it will be outside the influence of M_2.
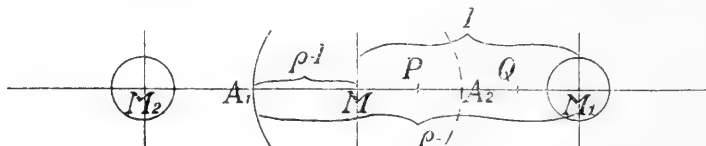
Fig. 2.

In the *third* place M can also be continually within the sphere of attraction of M_2 as soon as viz. M, on contact with M_1 (distance of the middle points $= s$), is still just on the edge of the sphere of attraction of M_2; i.e. when $A_2 M_1 = 2l - \varrho$ has just the value s. Then l is therefore $= \frac{1}{2} (\varrho + s)$. Thus in the second (transition) case $l > \frac{1}{2} (\varrho + s)$, while for the third case we have simply $l < \frac{1}{2} (\varrho + s)$. Now we found before (see the cited papers) ϱ to be about $1,7 \, s$.

We should then have: 1st case $l > 1,7\,s$; 2nd case $l < 1,7\,s > 1,35\,s$; 3rd case $l < 1,35\,s$.

At the critical temperature $v_k = 3,8\,b_0$ (at least for "ordinary" substances), hence $l = s\sqrt[3]{3,8} = 1,56\,s$ (the molecule thought to be cubical). Hence the *entire solid state and almost all liquid volumes*, starting from the melting point ($l = 1,08\,s$ about) to far above the boiling-point, are in the *third* case, every molecule being continually within the sphere of attraction of the neighbouring molecules. Only the volumes quite close to T_k, both the liquid and the vapour volumes, belong to the second (transition) case, and almost all the vapour volumes should be reckoned to the first case (see fig. 1).

When ϱ is taken still somewhat greater than $1,7\,s$, e.g. $= 2s$, the transition case lies between $2\,s$ and $1,5\,s$, and then comprises only the smallest vapour volumes in the neighbourhood of the critical point, while (practically) *all* the liquid volumes up to T_k, where $l = 1,56\,s$, belong to the third case.

We must now make a plausible supposition about the nature and the way of action of the attractive and repulsive forces, which supposition should also enable us to make the mathematical calculations easy to carry out. Among all the suppositions which I have tried with respect to the attractive forces on different occasions, now and before, the simplest is this that we assume the attraction to increase *from the sphere of attraction ϱ linearly* proportionate to the distance to that sphere. If e.g. the molecule is in the point P (fig. 2), the attraction that it undergoes from M would be $= f \times A_1 P$.

Instead, therefore, of supposing the attractive action to *decrease* from the centre of the molecule outwards to the edge of the sphere of attraction (according to a certain reciprocal power of the distance r to the centre, by e.g. putting $T = f : r^6$, or $T = (f : r^2) \times e^{-r/u}$, which renders the integrations always unfeasible or exceedingly complicated, and in consequence of which the attractive action at the edge of the sphere of attraction never becomes $= 0$), the reversed course is taken, and the attractive action is made to *increase* from the edge of the sphere of attraction *inwards*. The results will not differ much, but a great simplification of the calculations is reached. We shall only see quantitative differences appear on different suppositions about the attractive forces (in the numerical coefficients etc.), but the found form of the functions of temperature and volume will remain *qualitatively* unchanged. And it still remains the question whether our supposition, in connection with the assumption that the molecules and atoms are all electron-systems, is not at least as justifiable as the other above-mentioned suppositions.

As regards the *repulsive* forces on contact of the molecules, for them I assume the same thing as before (cf. among others loc. cit. I § 7 p. 856), namely that as soon as the molecule is compressed (the atoms or the electron rings pressed inward from their state of equilibrium), there is excited a quasi-elastic repulsive force, which (for not too great compressions) likewise increases *linearly* with the deviation from the state of equilibrium.

§ 3. Construction of the Fundamental Equations.

Hence in the *first* of the three above indicated cases $(l > \varrho)$, the attraction of M through M_1 (when $MQ = x$ is put in fig. 1) may be represented by $F = f \times A_1 Q$, i.e. by $f \times (MQ - MA_1)$, or by

$$F = f(x - (l - \varrho)).$$

In the integrations x is then to be taken from $l - \varrho$ to $l - s$.

In the *second* case $(l < \varrho > \frac{1}{2}(\varrho + s))$ in P (fig. 2) the attraction of M by M_1 is $f \times A_1 P = f \times (MP + A_1 M)$, whereas that which M experiences from M_2 is $= f \times PA_2 = f \times (MA_2 - MP)$. Hence, putting MP again $= x$, we get:

$$F_1 = f(x + (\varrho - l)) \quad ; \quad F_2 = f((\varrho - l) - x).$$

In this x must be taken between 0 and $l - s$ for F_1; for F_2 only between 0 and $\varrho - l$. If x becomes $> \varrho - l$, F_2 would become negative, i.e. P gets outside the sphere of attraction of M_2.

In the *third* case of course the same expressions hold as in the second case, but now x can also be taken between 0 and $l - s$ for F_2, $l - s$ now being $< \varrho - l$. $(2l < \varrho + s)$.

Throughout the *entire* path between $MP = 0$ and $MP = l - s$ we may thus write in this third case for the joint action $F = F_1 - F_2$, i.e.

$$F = f \times 2x.$$

It seems, therefore, *as if* the attractive action starts from the point M, and is proportional to double the distance from P to that neutral initial point, where in all the three cases mentioned the total action will, of course, be $= 0$.

We shall treat this last (third) case first, as it is by far the most important. We shall then be able to treat the two first cases in a simple way. The now following considerations, therefore, all refer to *small* volumes $(l < 1,35$ to $1,5 s$, i.e. $v < 2,5$ to $3,4 b_0)$, both for liquids and for solid bodies.

For the square of velocity u^2 in the point $P(MP = x)$ the following equation then holds:

$$u_x{}^2 = u_0{}^2 + \frac{2}{m} \int_0^x f \times 2x \, dx = u_0{}^2 + \frac{2f}{m} x^2 \quad . \quad . \quad . \quad . \quad (a)$$

On contact of the two molecules $u^2{}_{l-s}$ has therefore become

$$= u_0{}^2 + \frac{2f}{m} (l-s)^2, \text{ while } - \text{ in consequence of the appearance of}$$

the repulsive force, given by (the quasi-elastic force being represented by 2ε)

$$F' = 2\varepsilon \,(x - (l-s)),$$

when P is within the distance s (on contact) — the velocity is henceforth represented by

$$u_x{}^2 = u_0{}^2 + \frac{2f}{m} (l-s)^2 - \frac{2}{m} \int_{l-s}^x 2\,\varepsilon\,(x - (l-s))\,dx,$$

i.e. by

$$u_x{}^2 = u_0{}^2 + \frac{2f}{m} (l-s)^2 - \frac{2\varepsilon}{m} (x - (l-s))^2 \quad . \quad . \quad . \quad . \quad (b)$$

Hence we have, u being dx/dt :

$$dt_1 = \frac{dx}{\sqrt{u_0{}^2 + \dfrac{2f}{m} x^2}}; \quad dt_2 = \frac{dx}{\sqrt{u_0{}^2 + \dfrac{2f}{m}(l-s)^2 - \dfrac{2\varepsilon}{m}(x - (l-s))^2}};$$

i.e. for the times t_1 and t_2 resp. between M and the collision, and during the collision up to the culminating point, where u has become $= 0$:

$$t_1 = \int^{l-s} \frac{dx}{\sqrt{u_0{}^2 + \dfrac{2f}{m} x^2}}; \quad t_2 = \int_{l-s}^{l-s'} \frac{dx}{\sqrt{u_0{}^2 + \dfrac{2f}{m}(l-s)^2 - \dfrac{2\varepsilon}{m}(x - (l-s))^2}}, \quad . \quad (c)$$

when s' represents the distance of the molecule centres at the highest point of the compression.

For the *mean square of velocity*, i.e. the *time-average*, which also occurs in the *Virial equation*, and to which the *temperature* is proportional, we evidently have now quite generally :

$$\overline{u^2} = \frac{1}{t} \int_0^{l-s'} \left[u_0{}^2 + \frac{2f}{m} x^2 - \frac{2\varepsilon}{m} (x - (l-s))^2 \right] dt,$$

i.e. with

$$dt = \frac{dx}{\sqrt{u_0{}^2 + \dfrac{2f}{m} x^2 - \dfrac{2\varepsilon}{m} (x - (l-s))^2}},$$

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also :

$$\overline{u^2} = \frac{1}{t} \int_0^{l-s} \sqrt{u_0{}^2 + \frac{2f}{m} x^2 - \frac{2\varepsilon}{m}(x - (l-s))^2} \cdot dx,$$

when the two paths covered $x = 0$ to $l-s$, and $x = l-s$ to $l-s'$ are considered as one. Over the first range ε must be always taken as $= 0$, whereas over the second we must put $f = 0$. The above integration may now also be split up into two parts, and the following equation may be put :

$$\overline{u^2} = \frac{1}{t} \left[\int_0^{l-s} \sqrt{u_0{}^2 + \frac{2f}{m} x^2} \, dx + \right.$$

$$\left. + \int_{l-s}^{l-s'} \sqrt{u_0{}^2 + \frac{2f}{m}(l-s)^2 - \frac{2\varepsilon}{m}(x - (l-s))^2} \, dx \right] \qquad , \quad . \quad (d)$$

in which $t = t_1 + t_2$ may be put (see (c)). In the second integral x^2 has become constant and equal to $(l-s)^2$ for the part referring to the attraction, and it does not increase any further in consequence of the elimination of the attractive force. [1])

The importance of this last relation is very great. For if $\frac{1}{2} N m \overline{u^2}$ (N is the total number of molecules, e.g. in 1 Gr. mol.) is a measure for the *temperature* of the system, then $\frac{1}{2} N m u_0{}^2$ will be a measure for the *Energy* of that system. For only the velocity $u_0{}^2$, with which a molecule passes the neutral position in M, can be arbitrarily increased or decreased by addition or diminution of energy (heat). What is added to $\frac{1}{2} N m u_0{}^2$, in the term $N f(l-s)^2$ e.g. till the collision, in consequence of the attractive action of the molecules, can *never* be modified by supply or removal of energy. This

[1]) When we assume that the attractive action still continues to exist *during* the collision (which would even be plausible), $\frac{2f}{m} x^2$ should again be substituted for $\frac{2f}{m}(l-s)^2$ at the second integration in (c) and (d). But then the results become much more intricate, while the difference is after all exceedingly slight, because ε is so many times greater than f. The already very short period of time of the collision would only become *somewhat* longer, while also the mean square of velocity would be subjected to only a slight modification in its value. Hence we have relinquished the idea of working out this entirely unnecessary complication, the more so as the supposition concerning the mode of action of the attractive forces made by us (i.e. in direct ratio to the distance of the centre of the moving molecule to the edge of the sphere of attraction of one of the two other molecules between which it moves to and fro), should only be esteemed an approximation.

amount is *constant*, and can be represented by E_0; i. e. the Energy that remains when $u_e = 0$ (quite potential in the neutral point M; quite kinetic at the moment of the impact). Accordingly this quantity is what PLANCK and others have called the so-called *zero-point energy*, which is nothing but the energy of the attractive forces, which is also in connection with the quantity $^a/_v$ (Cf. also § 5).

Hence the quantities $\overline{u^2}$ and $u_0{}^2$ will always be very different according to (d) (only at high temperatures and large volumes there will practically be no difference), and for years I have already harboured the conviction that in this [1]) we should look for the clue of the remarkable relation between T and E drawn up by PLANCK for low temperatures and small volumes -- but which according to him can only be derived on the strength of very particular suppositions (the so-called hypothesis of *quanta*).

§ 4. Calculation of t and $\overline{u^2}$.

According to (c) we now find for t_1, putting $\dfrac{x}{u_0}\sqrt{\dfrac{2f}{m}} = y$:

$$t_1 = \int_0^{l-s} \frac{dx}{\sqrt{u_0{}^2 + \dfrac{2f}{m} x^2}} = \sqrt{\frac{m}{2f}}\ log\,(y + \sqrt{1 + y^2})_{x=0}^{x=l-s}\,,$$

which with

$$\varphi = \frac{l-s}{u_0}\sqrt{\frac{2f}{m}} \quad \cdots \quad \cdots \quad \cdots \quad (1)$$

leads to:

$$t_1 = \sqrt{\frac{m}{2f}}\ log\,(\varphi + \sqrt{1+\varphi^2}). \quad \cdots \quad \cdots \quad (2)$$

For $u_e = \infty$ $(\varphi = 0)$ this approaches to $t_1 = \sqrt{\dfrac{m}{2f}}\ log\,(\varphi + 1) =$

$= \varphi\sqrt{\dfrac{m}{2f}} = \dfrac{l-s}{u_0}$, as was to be expected. The time is then scarcely shortened by the attractive action. But when u_0 approaches 0 $(\varphi = \infty)$,

t_1 approaches $\sqrt{\dfrac{m}{2f}}\ log\,2\varphi = \sqrt{\dfrac{m}{2f}}\ log\left(\dfrac{l-s}{u_0}\sqrt{\dfrac{2f}{m}}\right)$, which thus approaches logarithmically infinite. This is owing to this, that when

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[1]) Apart of course from the interpretation of the quantity $h\nu$ occurring in . PLANCK's formula, in which h is a universal constant — which forms an *entirely separate* problem.

u_0 is exceedingly small, the time in which the very first part of the path close to the neutral point M is passed over will be very great, in spite of the attractive action (which will then, however, be still very small). We shall presently see that it is *this* circumstance which leads to the essential element of PLANCK's relation, viz. to the logarithmical approach (in direct ratio to $1 : log\dfrac{1}{u_0}$) to 0 of $\overline{u^2}$ (i. e. of T), when u_0^2 (i. e. $E - E_0$) approaches to 0. The time integral $\int u^2\, dt$ remains namely *finite* (in consequence of the attractive action the exceedingly slight value of u_0^2 increases to a finite value), notwithstanding t itself approaches (logarithmically) to infinite.

Further we now find for t_2 with

$$y = (x - (l-s))\sqrt{\dfrac{2\varepsilon}{m\left(u_0^2 + \dfrac{2f}{m}(l-s)^2\right)}} :$$

$$t_2 = \int_{l-s}^{l-s'} \dfrac{dx}{\sqrt{u_0^2 + \dfrac{2f}{m}(l-s)^2 - \dfrac{2\varepsilon}{m}(x-(l-s))^2}} = \sqrt{\dfrac{m}{2\varepsilon}}\,(Bg\,sin\,y)_{l-s}^{l-s'} =$$

$$= \sqrt{\dfrac{m}{2\varepsilon}}\,Bg\,sin\left\{(s-s')\sqrt{\dfrac{2\varepsilon}{m(u_0^2 + etc\,)}}\right\}.$$

But in consequence of the relation

$$u^2 = u_0^2 + \dfrac{2f}{m}(l-s)^2 - \dfrac{2\varepsilon}{m}(s-s')^2 = 0$$

at the culminating point of the collision (see equation (b)), the quantity under $Bg\,sin$ will be exactly $= 1$, so that:

$$t_2 = \tfrac{1}{2}\pi\sqrt{\dfrac{m}{2\varepsilon}}\,, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

the known expression for the time of vibration under the influence of the quasi-elastic repulsive action, proportional to the deviation from the state of equilibrium. (That here $^1/_2\,\pi$ occurs instead of $2\,\pi$, is owing to this that only a fourth part of the entire oscillation is considered. (see above)).

We shall now compute the value of $\overline{u^2}$ according to (d). The first integral within [ ] gives:

$$I_1 = \int_0^{l-s} \sqrt{u_0{}^2 + \frac{2f}{m} x^2}\, dx = u_0{}^2 \sqrt{\frac{m}{2f}} \int_{x=0}^{x=l-s} \sqrt{1 + y^2}\, dy,$$

when again, like above, $\dfrac{x}{u_0} \sqrt{\dfrac{2f}{m}} = y$ is put. Hence we get:

$$I_1 = u_0{}^2 \sqrt{\frac{m}{2f}} \times \tfrac{1}{2} \left[\sqrt{1+y^2} - log\left(-y + \sqrt{1+y^2} \right) \right]_{x=0}^{x=l-s}.$$

The lower limit gives 0; for the upper limit y again passes into φ, so that we have:

$$I_1 = \tfrac{1}{2} u_0{}^2 \sqrt{\frac{m}{2f}} \left[\varphi \sqrt{1+\varphi^2} - log\left(-\varphi + \sqrt{1+\varphi^2} \right) \right] \quad . \quad . \quad (4)$$

The second integral becomes:

$$I_2 = \int_{l-s}^{l-s'} \sqrt{u_0{}^2 + \frac{2f}{m}(l-s)^2 - \frac{2\varepsilon}{m}(x - (l-s))^2}\, dx =$$

$$= \left\{ u_0{}^2 + \frac{2f}{m}(l-s)^2 \right\} \sqrt{\frac{m}{2\varepsilon}} \int_{x=l-s}^{x=l-s'} \sqrt{1 - y^2}\, dy,$$

in which now $y = \dfrac{x-(l-s)}{\sqrt{u_0{}^2 + \dfrac{2f}{m}(l-s)^2}} \sqrt{\dfrac{2\varepsilon}{m}}$. We further find,

therefore:

$$I_2 = \left\{ u_0{}^2 + \frac{2f}{m}(l-s)^2 \right\} \sqrt{\frac{m}{2\varepsilon}} \times \frac{1}{2} \left[y\sqrt{1-y^2} + Bg \sin y \right]_{x=l-s}^{x=l-s'}.$$

For the lower limit y becomes $= 0$, and everything disappears, so that we only retain:

$$I_2 = \tfrac{1}{2} \left\{ u_0{}^2 + \frac{2f}{m}(l-s)^2 \right\} \sqrt{\frac{m}{2\varepsilon}} \left[\varphi' \sqrt{1-\varphi'^2} + Bg \sin \varphi' \right],$$

when $\dfrac{s-s'}{\sqrt{u_0{}^2 + \dfrac{2f}{m}(l-s)^2}} \sqrt{\dfrac{2\varepsilon}{m}} = \varphi'$ is put. However, in conse-

quence of the relation

$$u^2 = u_0{}^2 + \frac{2f}{m}(l-s)^2 - \frac{2\varepsilon}{m}(s-s')^2 = 0$$

at the culminating point of the collision (see above) φ' will evidently be $= 1$, so that we finally get:

$$I_2 = \tfrac{1}{2} u_0{}^2 (1+\varphi^2) \sqrt{\frac{m}{2\varepsilon}} \times \tfrac{1}{2} \pi \quad . \quad . \quad . \quad . \quad . \quad (5)$$

These are, accordingly, the two *time integrals* of the square of velocity u' before and during the collision.

Hence we shall have for the mean square of velocity $u^2 = \dfrac{I}{t} = \dfrac{I_1 + I_2}{t_1 + t_2}$,

$$\bar{u}^2 = \tfrac{1}{2} u_0^2 \frac{\sqrt{\dfrac{m}{2f}}\left[\varphi \sqrt{1+\varphi^2} - log\left(-\varphi+\sqrt{1+\varphi^2}\right)\right] + \tfrac{1}{2}\pi \sqrt{\dfrac{m}{2\varepsilon}}(1+\varphi^2)}{\sqrt{\dfrac{m}{2f}} log\left(\varphi + \sqrt{1+\varphi^2}\right) + \tfrac{1}{2}\pi\sqrt{\dfrac{m}{2\varepsilon}}}, \quad (6)$$

being with $\varphi = \dfrac{l-s}{u_0}\sqrt{\dfrac{2f}{m}}$ the required expression for u^2, expressed in u_0^2, and which will be valid for *small* volumes ($< v_k$) for *all* temperatures.

§ 5. Two Important Limiting Cases.

a. High temperatures.

For $u_\bullet = \infty\,(\varphi = 0)$ we now get:

$$\bar{u}^2 = \tfrac{1}{2} u_0^2 \frac{\sqrt{\dfrac{m}{2f}} \cdot 2\varphi + \tfrac{1}{2}\pi\sqrt{\dfrac{m}{2\varepsilon}}}{\sqrt{\dfrac{m}{2f}} \cdot \varphi + \tfrac{1}{2}\pi\sqrt{\dfrac{m}{2\varepsilon}}},$$

as $- log\left(-\varphi+\sqrt{1+\varphi^2}\right)$ then approaches to $- log\left(1-\varphi\right) = \varphi$, and likewise $log\left(\varphi + \sqrt{1+\varphi^2}\right)$ and $\varphi\sqrt{1+\varphi^2}$. For φ near 0 the first terms will be cancelled by the second, and u^2 will, therefore, approach to

$$(T = \infty) \qquad \bar{u}^2 = \tfrac{1}{2} u_0^2, \quad \ldots \ldots \ldots (7)$$

so that the time average of the square of velocity for small volumes and *high* temperatures amounts to only half the square of velocity in the neutral point. In consequence of the disappearance of the terms with f by the side of those with ε the time average is namely chiefly formed by the *diminution* of velocity *during the collision*, and not by the increase before the impact in consequence of the attraction. This latter increase lasts so short that it may be neglected with respect to the subsequent important diminution of velocity (down to 0).

Now for a linear system $Nm\,\bar{u}^2$ is not $= 3RT$, but simply $= RT$, and in the general relation

$$\tfrac{1}{2} N m\, u^2_{l-s} = \tfrac{1}{2} N m\left(u_0^2 + \frac{2f}{m}(l-s)^2\right)$$

for the vis viva at the beginning of the collision, i.e. for the sum

of kinetic and potential energy in the neutral point M (hence in all the points of the path passed over by M) the quantity $^1/_2 N m \, u^2{}_{l-s}$ does not represent the whole spacial Energy E, but only $^1/_3$ part of it. Likewise $N f (l-s)^2$ will not represent the whole energy of attraction [1]) (zero point energy) E_0, but again $^1/_3 E_0$ [2]). Hence we may put:

$$N m \, \overline{u^2} = RT \quad ; \quad ^1/_2 N m \, u_0{}^2 = ^1/_3 (E-E_0),$$

so that according to (7) we have at high temperature:

$$(T = \infty) \qquad RT = \tfrac{1}{3}(E-E_0) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

That this equation is correct, appears from this that it gives for c_v:

$$(T = \infty) \qquad c_v = \frac{dE}{dT} = 3R = 6$$

in gr. cal., hence the expected *double* heat capacity, which is only $= 3$ for large volumes (gases) under the same circumstances (i.e. high temperatures) — always on the supposition of *mon-atomic* substances, as otherwise the internal energy of the atoms within the molecules will still be added to E.

We still point out, that when the molecules were *perfectly rigid* systems, hence could not be pressed in, the quantity ε in our formula (6) for $\overline{u^2}$ would be *infinitely great*, and therefore the duration of collision absolutely $= 0$, so that then not the first terms with

$$\sqrt{\frac{m}{2f}} \cdot \varphi \quad \text{would be cancelled by the second with } \tfrac{1}{2}\pi \sqrt{\frac{m}{2\varepsilon}},$$

when φ approaches 0, but *just the reverse*: these latter terms would disappear by the side of the former, however small these might be on account of φ. But accordingly then $\overline{u^2}$ will not become $= ^1/_2 u_0{}^2$, but $= u_0{}^2$, hence $RT = ^2/_3 (E-E_0)$, so that $c_v =$ would become $^3/_2 R = 3$ and not $= 6$. That, therefore, the capacity of heat for condensed systems does not *approach to* 3 *but to* 6, is a proof that the molecules may *not* be considered as perfectly rigid spheres, but are *elastic* systems, liable to *compression*, in which the *time of*

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[1]) We point out that for the limiting volume $v = b$ $(l = s)$ our $E_0 = 3 N f (l-s)^2$ will approach to 0. In fact, as all movement is then impossible, the energy $^3/_2 N m \, u^2$ can in this case not undergo any increase in consequence of the work of attraction. Of course by the side of the E_0 introduced by us, another zero point energy may always be introduced, which is in connection with that of the atoms (systems of electrons) *within* the molecule. The formulae are, however, not modified by this in any respect.

[2]) Division by 3 can also be justified by this that for the linear systems considered by us the velocities are all velocities u_n directed *normally* with respect to the molecules. And now $\overline{u_n{}^2} = ^1/_3 \overline{u^2}$.

collision is not infinitely small or negligibly small, but will have a certain, though small, yet *finite* value.

It is self-evident that as soon as φ is no longer near 0, but assumes some value (T no longer very high), $\overline{u^2}$ will very soon rise to higher values than $\frac{1}{2} u_0^2$ in consequence of the increasing influence of the terms with φ, hence c_v will decrease from 6 to lower values.

§ 6. *b.* Low Temperatures.

At low and very low temperatures u_0 will approach to 0, i.e. φ to ∞. The general equation (6) then passes into

$$\overline{u^2} = \frac{1}{2} u_0^2 - \frac{\sqrt{\frac{m}{2f}}\left[\varphi^2 - log\left(-\varphi + \varphi\left(1 + \frac{1}{2\varphi^2}\right)\right)\right] + \frac{1}{2}\pi\sqrt{\frac{m}{2\varepsilon}}\varphi^2}{\sqrt{\frac{m}{2f}}\ log\left(2\varphi + \frac{1}{2\varphi}\right)},$$

in which in the denominator the very small time of the collision may be neglected by the side of the time that approaches logarithmically infinite under the influence of the attractive forces. Thus we get with $- log (1 : 2\varphi) = log\ 2\varphi$, and after division in numerator and denominator by $\sqrt{\frac{m}{2f}}$:

$$\overline{u^2} = \frac{1}{2} u_0^2 \cdot \frac{\left(1 + \frac{1}{2}\pi\sqrt{\frac{f}{\varepsilon}}\right)\varphi^2 + log\ 2\varphi}{log\left(2\varphi + \frac{1}{2\varphi}\right)}.$$

But in first approximation also $\frac{1}{2}\pi\sqrt{\frac{f}{\varepsilon}}$ may now be neglected by the side of 1 in the numerator, as ε will then be so many times greater than f. And besides $log\ 2\varphi$ may be neglected by the side of φ^2, when φ approaches ∞. Hence we finally get:

$$(T = 0)\quad \overline{u^2} = \frac{1}{2} u_0^2 \frac{\varphi^2}{log\left(2\varphi + \frac{1}{2\varphi}\right)} = \frac{u_0^2\ \varphi^2}{log\ (4\varphi^2 + 2)}, \quad \cdot \quad (9)$$

in which φ^2 is $= \frac{(l-s)^2}{u_0^2} \cdot \frac{2f}{m}$ (cf. (1) in § 4). From this it already appears that the ratio between $\overline{u^2}$ and u_0^2 will approach ∞, i.e. likewise the ratio $RT : (E - E_0)$. For φ^2 is infinitely great with respect to $log\ \varphi^2$. However, $\overline{u^2}$ itself will also approach to 0, as $u_0^2\ \varphi^2$ remains *finite* (see also the beginning of § 4). But while the time,

during which the path is covered under the influence of the attraction, approaches logarithmically infinite, $\overline{u^2}$ does not then approach 0 ordinarily in the same way as $u_0{}^2$, but to a *much slighter degree*, proportionally to $1 : log \dfrac{1}{u_0{}^2}$. I.e. the *temperature* will approach 0 much more slowly than the Energy; when the temperature still has a very small value, the "Energy" (i.e. $E-E_0$) will practically be already $= 0$. The latter, namely, is only determined by $u_0{}^2$ in the neutral point, whereas the temperature is determined by the time average of the square of velocities which has *increased* under the influence of the attraction.

Hence relatively only exceedingly little supply of energy is required to augment the temperature by a certain amount: in other words *the heat capacity will rapidly approach* 0 *at low temperatures*.

When we substitute its value for φ^2, $u_0{}^2 \varphi^2$ becomes $= \dfrac{2f}{m}(l-s)^2$, so that with $Nf(l-s)^2 = {}^1/_3 E_0$ and $Nm\,\overline{u^2} = RT$ (see above) we get:

$$(T=0) \quad RT = \frac{{}^2/_3\,E}{log\left(\dfrac{4E_0}{E-E_0} + 2\right)}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10)$$

as $\varphi^2 = \dfrac{2Nf\,(l-s)^2}{Nm\,u_0{}^2} = \dfrac{{}^1/_3\,E_0}{{}^2/_3\,(E-E_0)} = \dfrac{E_0}{E-E_0}$.

Accordingly, by (10) T is expressed in E for the case of small volumes and low temperatures. It is noteworthy that (10) is not *quite* identical with PLANCK's relation, but that the *logarithmically infinite* denominator $log\,(4\varphi^2 + 2) = log\left(\dfrac{4E_0}{E-E_0}+2\right)$ would have to be diminished by the *small finite* quantity $log\,2 = 0,69$, in consequence of which the denominator would become $log\,(2\varphi^2 + 1) = log\left(\dfrac{2E_0}{E-E_0}+1\right)$. The original denominator $log\left(2\varphi + \dfrac{1}{2\varphi}\right)$ would, therefore, have to be diminished by ${}^1/_2\,log\,2 = 0.35$.

Different circumstances might be adduced as an explanation of this exceedingly slight difference, which is for the rest immaterial. First of all possibly an exceedingly small modification in our fundamental suppositions concerning the mode of action of the attractive forces, the logarithmic form of t_1 being retained, might give rise to a modification in this sense that still a constant term is to be applied. And in the second place the taking in account of MAXWELL's distri-

bution-law of velocities in the calculation of t_1 may have a certain influence on the result. Unfortunately the computations referring to this cannot be executed, because they will lead to a definite integral which cannot be determined. In the third place it may be alleged that with respect to the velocity of the moving molecule M it is not quite justifiable to assume the molecules M_1 and M_2 to be *at rest* on the strength of the fact that the movement may be directed equally well towards the left as towards the right. It should be pointed out here that when M_1 e.g. is on the lefthand side of its mean position, it will exert a stronger attractive action on M than when it is on the righthand side. And there are more similar remarks that might be made.

In virtue of the above considerations we may, therefore, safely apply the said correction, which is exceedingly slight with respect to the logarithmically infinite chief term, and write:

$$RT = \frac{{}^2/_3 E_0}{log\left(\frac{2E_\bullet}{E-F_0} + 1\right)} \quad \ldots \ldots \quad (10a)$$

When we reverse this relation, we get:

$$E-E_0 = \frac{2E_0}{e^{\frac{{}^2/_3 E_0}{RT}} - 1} \quad \ldots \ldots \ldots \quad (11)$$

Putting in this:

$$E_0 = 3 N f (l-s)^2 = {}^3/_2 N \cdot hv \cdot \quad \ldots \ldots \quad (12)$$

we get finally:

$$E = \tfrac{3}{2} N hv + \frac{3 N hv}{e^{\frac{N hv}{RT}} - 1}, \quad \ldots \ldots \quad (11a)$$

which is in agreement with PLANCK's relation (after muliplication by 3 on account of the transition from a linear to a spacial oscillator).

Hence the quantity hv introduced by PLANCK would have been given by:

$$hv = 2 f (l-s)^2, \quad \ldots \ldots \ldots \quad (11a)$$

from which h could be calculated when v is *determined* (this quantity v would, accordingly, have to contain the factor $(l-s)^2$, hence it would be dependent on the *volume*, as is, indeed, assumed), and when f, the constant of the attractive action introduced by us, is known. We shall return to this *special* problem later on.

We only still point out that our formula (11) or (11a), resp. (10) or (10a) is only valid for *low*, and *not* for high temperatures, whereas

PLANCK is of opinion that the expression (11a) is of general application, for high as well as for low temperatures. According to our derivation the more complicated [1]) formula (6) would represent the generally valid relation, which is only transformed to the form (11a) for very low temperatures.

Christmas 1918. · (*To be continued*).

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[1]) Also EINSTEIN, DEBYE and others already derived more complicated relations, which are considered to represent the relations better than PLANCK's simple formula.

Chemistry. — "Eykman's *Refractometric Investigations, in Connection with the Presentation of the Edition of his Works."* By Prof. A. F. Holleman.

Though Eykman devoted about twenty-five years of his life to refractometric investigations of organic compounds, and collected in the course of these researches a tremendous amount of material, arriving at very important conclusions from this material, his work in this interesting region has, nevertheless, remained pretty well unknown. This is chiefly owing to the way in which he published it.

At first choosing for this purpose the Berichte der deutschen chemischen Gesellschaft, he afterwards wrote a number of treatises in the Recueil; but by far the greater part of his papers appeared exclusively in the Chemische Weekblad.

The researches of his pupils were up to now only laid down in Theses for the Doctorate.

For foreign chemists, who are only by exception conversant with the Dutch language, it was, therefore, practically impossible, to get acquainted with Eykman's researches.

It further appeared, when his posthumous papers were put into my hands by his brother, our fellow-member Chr. Eykman, that these contained still a voluminous material of facts which had not yet been published at all.

In order to render his ideas and experimental results more generally accessible, it was necessary to collect his refractometric researches and publish them as a whole. This publication has been rendered possible by the financial help of the Hollandsche Maatschappij der Wetenschappen, which in this has proved itself worthy of its high traditions.

In the now published work: Recherches réfractométriques de feu J. F. Eykman, are found in the first place a biography and a summary of his researches in this region. Then follow the papers from the "Berichte", which contain among others his researches on the displacement of the double bindings in the side chains of aromatic compounds towards the nucleus. This displacement gives rise to a considerable increase of the molecular refraction and dispersion.

In his papers in the Recueil he described the refractometer constructed by him with constant deviation of 40°, which is obtained by rotation of the prism round a vertical axis. This apparatus has further an appliance, by means of which measurements of the refraction up to a temperature of about 150° can take place with ease for which reason it is to be preferred for organic-chemical researches to all other refractometers. Also his pycnometers are described there.

It is further demonstrated in these papers that the refractometric value of the group CH_2 is constant for the most divergent homologous series, if only the first three terms of these series are left out of consideration, for which this value is either greater or smaller.

Besides they contain the derivation of EYKMAN's formula for the molecular refraction. Hitherto the formula of GLADSTONE and DALE: $\dfrac{n-1}{d}$. $P = const.$ was generally used for this, in which n represents the index of refraction, d the specific weight of the liquid substance, and P the molecular weight. After the formula $\dfrac{n^2-1}{n^2+2} \cdot \dfrac{P}{d}$ had been derived by LORENTZ by a theoretical way, this formula got to be almost exclusively used. The formulae of GLADSTONE and DALE and of LORENTZ do not present a constant value, however, for large ranges of temperature (e.g. of 100°); but those of the former descend, while the theoretical formula gives ascending values.

Taking into account that G. & D's formula may also be written: $\dfrac{n^2-1}{n+1} \cdot \dfrac{P}{d}$, and that accordingly the difference between the two formulae refers only to the denominator, EYKMAN tried by an empirical way to find a formula that also has constant values for large ranges of temperatures, and he found it in the expression $\dfrac{n^2-1}{n+0.4} \cdot \dfrac{P}{d}$. This rendered it, therefore, possible, to directly compare measurements which have been made at very divergent temperatures.

The papers in the Chemisch Weekblad treat two problems of great importance for organic refractometry, viz.: the cyclic compounds and unsaturate substances. As far as the former is concerned, he comes to the result that the number of C-atoms in the nucleus has a considerable influence on the refraction, which also extends over the refractometric values which CH_2-groups have in the side chain.

In reference to the unsaturate compounds he proves by means of an exceedingly copious material, that there can be no question of a constant increment for the double binding, which BRÜHL intro-

duced, for that the double binding can exert a very divergent influence on the refraction, and especially on the dispersion of unsaturate compounds.

Among the posthumous papers there were the refractometric determinations of more than 350 compounds, which had not yet been published, among which almost complete series of homologues. That EYKMAN did not publish these himself I attribute chiefly to the fact that he could less and less bring himself to prepare his results for the press. Possibly, too, he wished to wait till some series had become still more complete, or to repeat some measurements before their publication. In view of these surmises it may seem somewhat bold to make results public which the master himself thought fit to withhold still. Besides, however, the fact mentioned just now, there is another circumstance that justifies publication. It is the comparison of the measurements made at the same substances which were carried out by him in many successive years. Then there appears to exist an almost perfect agreement in the values in almost all cases. In fact all his work gives the impression of having been executed with scrupulous care, also as regards the purity of the compounds.

It is to be regretted that the material left behind consists almost exclusively of tables, without any commentary. I have tried to supply this defect by adding a review to every series of measurements of homologues, for the rest fully realising the difficulty of this task, which certainly would have been accomplished by the master himself in a much better way. I have set myself the task to interpret the results in these reviews as much as possible in the same spirit as speaks from EYKMAN's works, which often give evidence of entirely different views from those embraced by most chemist who work in this field, in the hope that those who are more competent in this kind of researches will judge that I have succeeded in giving the right interpretation.

The measurements left behind comprise compounds from the following homologous series: saturate hydrocarbons, alcohols $C_nH_{n21+}OH$, alkylhaloids, aliphatic and cyclic amines, acid $C_nH_{2n}O_2$ and their esters, saturate aldehydes and ketones, unsaturate hydro-carbons, unsaturate acids, plurivalent alcohols, pluribasic acids, hydroxy-acids, aldehydic and ketonic acids, derivatives of carbonic acid, cyclic compounds, aromatic hydro-carbons, phenols, aromatic amines and aromatic acids.

This posthumous material confirms on one side for the greater part the conclusions at which EYKMAN had already arrived by the

aid of what had been published by him, but it tests them by a number of compounds hitherto unknown; on the other side some new points of view have come to light. Among these we may mention the influence of the bifurcation of the carbon chains, the further differentiation of the atomic refraction of oxygen, the influence of stereo-isomery, and the closer inquiry into the dispersion of the organic compounds.

This entire posthumous work shows with great evidence that there can be no question of constant atom refractions, not even for carbon. Though the variations in the atom refractions of this element are often pretty insignificant, it yet does not constitute an exception to the general rule that the atom refractions are *not* constant.

EYKMAN's work aims at no less than a total revision of the refractometry of organic compounds; he has treated in a masterly way all the fundamental questions in this region, thanks to his great gifts of research and his amazing energy, which have fortunately remained unaffected under the depressing feeling of neglected merit.

Amsterdam, January 1919.

Chemistry. — *"On an Indirect Analysis of Gas-Hydrates by a Thermodynamic Method and Its Application to the Hydrate of Sulphuretted Hydrogen."* I. By Prof. F. E. C. Scheffer and G. Meyer. (Communicated by Prof. Böeseken).

(Communicated in the meeting of February 22, 1919).

I. In two papers one of us has given an extensive description of heterogeneous equilibria in the system sulphuretted hydrogen-water [1]). It has appeared in this investigation that through the appearance of a compound and through unmixing in the liquid state a four-phase equilibrium hydrate of sulphuretted hydrogen — two liquid layers – gas occurs in this system; the three-phase-lines which intersect in this quadruple point, were determined, and besides a number of analyses was carried out to get to know the composition of the hydrate. These analyses, however, yielded very different results; the number of molecules of water which is bound with one molecule of sulphuretted hydrogen varies between 5,1 and 5,5 according to these determinations. This result led to the conclusion that the formula of the hydrate would be $H_2S . 5H_2O$, because for this substance, and for gas hydrates in general a phenomenon occurs that causes the water content on analysis to be found too high. When we consider that the two liquid layers consist almost of pure sulphuretted hydrogen, resp. pure water, and that therefore, the hydrate must be formed by cooperation of the two liquid layers, it is clear that this formation of hydrate gives rise to a separation of the layers on the boundary of the liquids. In analyses an excess of sulphuretted hydrogen was always used, which was pumped off after action of the liquid layers. It is clear that when this excess of sulphuretted hydrogen has been removed, water can be left behind in the solid substance, as this possesses hardly any tension at low temperature as ice; this is accordingly the reason that formerly always lower values were found for the water content as more care was devoted to the interaction of the layers. Chronologically arranged the analyses yielded water contents of 15 [2]), 12 [3]) and 7 [4]) molecules

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[1]) These Proceedings. **13**. 829 (1911) and **14**. 195 (1911).
[2]) De Forcrand. C.r. **94**. 967. (1882).
[3]) De Forcrand. Ann. chim. phys. (5). **28**. 5. (1883).
[4]) De Forcrand and Villard. C.r. **106**. 1402. (1888).

of water per molecule of sulphuretted hydrogen. In the above-mentioned determinations this content had fallen to 5,1—5,5, and the conclusion was obvious that the true water content would be lower: $H_2S . 5H_2O$ was therefore the most probable formula on the ground of these experiments.

2. As direct analysis yielded dubious results, and the formula $H_2S . 5H_2O$ can only be considered probable on account of the observed disturbance — there were no indications pointing to a second disturbance in opposite sense — we have tried to find a method of analysis that yielded more certain results.

Indications to a definite formula that did not rest on direct analysis are the following:

a. VILLARD deems the formula $H_2S . 6H_2O$ probable on account of the analogy with other gas hydrates, for which he has drawn up a formula $M . 6H_2O$ [1]). This analogy must certainly be supported by a closer proof, before it convinces us of the accuracy of the said composition.

b. VILLARD could seed the two liquids at temperatures at which the hydrate can form, with the hydrate of N_2O and this leads him to the conclusion that the hydrate of sulphuretted hydrogen will possess the same water content [1]). This reason, too, makes him consider the formula $H_2S . 6H_2O$ probable.

c. DE FORCRAND makes use of a rule holding for three-phase lines, which is analogous to that of TROUTON for liquid-gas equilibria [2]). This rule may be represented as follows. When the three-phase line of a dissociating compound, which splits up into solid-gas, reaches a vapour tension of one atmosphere, the quotient of the heat of transformation and the absolute temperature has the value 30. He gives some examples for this rule, and then applies it to determine the quantity of water in gas hydrates. That this rule is, however, dangerous appears already sufficiently from the fact that on application to the hydrate of sulphur dioxide the composition $SO_2 . 8H_2O$ was found, whereas on the strength of BAKHUIS ROOZEBOOM's and VILLARD's analyses it could be concluded with great probability that this water-content is too high [3]). His rule, likewise, leads to $H_2S . 6H_2O$.

As in our opinion the indirect methods have not yet yielded certain results either concerning the composition of the hydrate, we have tried

[1]) VILLARD. Ann. chim. phys. (7). **11**. 289. (1897).
[2]) DE FORCRAND. C.r. **135**. 959. (1902).
[3]) BAKHUIS ROOZEBOOM. Rec. **3**. 29. (1884); VILLARD. Ann. chim. phys. (7). **11**. 289. (1897).

to find another for a long time. We think we have found a method that enables us to find the composition of the gas-hydrates with great certainty, of which the description follows below.

3. In order to make the principle on which this analysis rests, as clear as possible, we will imagine a binary system, of which the first component (A) is gaseous in a definite temperature range, the second (B) is in the neighbourhood of its melting-point under the same circumstances and not perceptibly volatile. On increase of pressure a solid compound can form from the gaseous first and the solid second component. In the melted second component the gas is soluble neither as such nor as compound. Then the P–T projection of the spacial figure is represented by figure 1. Hence the first component A appears in these equilibria in free state as a gas (G) and bound in the compound (S). The second component B occurs free as solid (S_B) and liquid (L), bound to the first component in the compound (S).

The three-phase lines $S_B LG$ and $SS_B L$ coincide with the melting-point line of B. The transformation is namely indicated by $S_B \rightleftarrows L$ on both three-phase lines, and is the same as on the melting-point line of pure B. The triple-point of B (point B in fig. 1) lies near
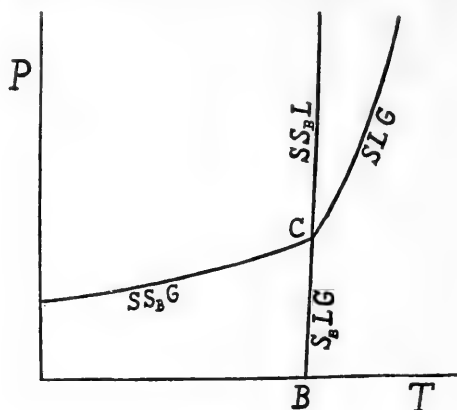
Fig. 1.

the T-axis; the sublimation – and the boiling-point line of B practically coincide with the T-axis.

When we indicate the compound by AB_n, the transformations on the two other three-phase lines are indicated by:

$$AB_n \rightleftarrows A + nB - E_1 \qquad \text{(on } SS_B G)$$
$$\text{(solid)} \quad \text{(gas)} \quad \text{(solid)}$$

$$AB_n \rightleftarrows A + nB - E_2 \qquad \text{(on } SLG).$$
$$\text{(solid)} \quad \text{(gas)} \quad \text{(liquid)}$$

Hence the difference between the two transformation energies E_1

and E_2 amounts to the melting energy or melting heat of n molecules B. When the heat of melting of one molecule B is indicated by Q, we get:

$$E_2 - E_1 = nQ \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

When we apply the equation of CLAPEYRON to the two three-phase equilibria, the indices 1 resp. 2 again referring to the equilibria SS_BG resp. SLG, the following relations follow:

$$T\frac{dP_1}{dT} = \frac{Q_1}{\Delta V_1} \quad \text{and} \quad T\frac{dP_2}{dT} = \frac{Q_2}{\Delta V_2} \quad . \quad . \quad , \quad . \quad (2)$$

in which Q_1 and Q_2 represent the heats of transformation.

When V_S and V_L are neglected with respect to V_G, which is allowed, when the density of the gas phase is small with respect to that of the other phases (pressure of the quadruple point C smaller than or in the neighbourhood of one atmosphere) and when the law of BOYLE is applied to the gas phase, we get:

$$T\frac{dP_1}{dT} = \frac{Q_1}{RT}P_1 \quad \text{and} \quad T\frac{dP_2}{dT} = \frac{Q_2}{RT}P_2 \quad . \quad . \quad . \quad . \quad (3)$$

From this follows on integration on the assumption that Q_1 and Q_2 are no functions of the temperature [1]:

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[1] This assumption indicates that the algebraic sum of the specific heats (that of the gas at *constant pressure*) of the substances participating in the transformation is zero. This is easily seen for the equilibrium liquid-gas on the following consideration. From the equation of Clausius $\frac{dQ}{dT} = h - H + \frac{Q}{T}$, in which h and H represent the specific heats of gas and liquid along the boundary line (VAN DER WAALS—KOHNSTAMM. Thermodynamik. I. S 67) and from the equation $h = c_v + T\left(\frac{dP}{dT}\right)_v\left(\frac{dv}{dT}\right)_{gr}$ (Ibid. I. S. 34, Gl. IIa; the index gr denotes that $\frac{dv}{dT}$ is measured along the boundary line) follows $\frac{dQ}{dT} = c_v - H + T\left(\frac{dP}{dT}\right)_v\left(\frac{dv}{dT}\right)_{gr} + \frac{Q}{T}$. If the law of Boyle holds good for the gas phase, the two last terms of the second member of this equation can be replaced by R and we get $\frac{dQ}{dT} = c_p - H$. We derive in an analogous way that a similar formula also holds for the three-phase equilibria described in the text.

When the algebraic sum of the specific heats differs from zero, the integrated equation 4 may only be used for a small range of temperature; then the heat of transformation at the quadruple point must be calculated from the found value of Q. A simular calculation follows in the discussion of the quantitative data. We may point out in conclusion that if Q is no temperature function, the energy of transformation, which is RT smaller, *does* depend on the temperature. The variation in E, caused by this correction is generally small with respect to the values of Q and E. (See tables with the quantitative data in the following paper).

$$ln\ P_1 = -\frac{Q_1}{RT} + C_1 \quad \text{and} \quad ln\ P_2 = -\frac{Q_2}{RT} + C_2 \ . \ . \ \textbf{(4)}$$

From a graphical representation $ln\ P_1 = f_1(T^{-1})$ and $ln P_2 = f_2(T^{-1})$ the slopes of the two straight lines can then be determined. Then the tangent of the angle of inclination amounts to $-\frac{Q_1}{R}$ resp. $-\frac{Q_2}{R}$. The difference multiplied by R yields the heat of melting $Q_2 - Q_1$, which is equal here to the energy of melting $E_2 - E_1$ [1]), and from this follows by the aid of equation (1) the value of n and with it the composition of the hydrate.

Accordingly for the application of this method of analysis the three-phase lines SS_BG and SLG must be experimentally determined.

4. The system sulphuretted hydrogen-water presents great analogy with the ideal system of § 3. As was demonstrated in the above-mentioned papers by one of us, a quadruple point SL_1L_2G appears in this system, indicated in fig. 2 by D. The stable part of the
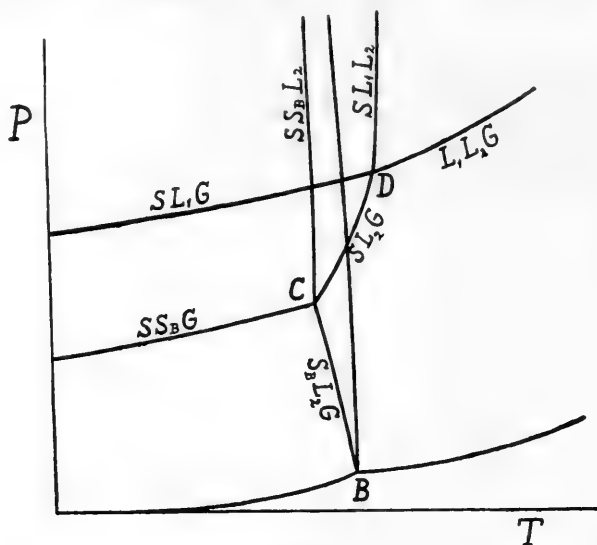
Fig. 2.

three-phase line SL_2G, a number of points of which was already deter-mined before [2]), terminates in the quadruple point SS_BL_2G, indicated in

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[1]) It appears from the transformations given in § 3 that $Q_1 = E_1 + RT$ and $Q_2 = E_2 + RT$, as one gramme molecule of gas is formed in both conversions. It follows from this that $Q_2 - Q_1 = E_2 - E_1$. The volumes of solid and liquid are neglected by the side of these of gas, and the expansion at melting does not cause an appreciable difference between melting energy and heat.

[2]) These Proceedings. **13**. 829 (1911).

fig. 2 by C. Through this quadruple point passes also the three-phase line SS_BG, and we shall now show that the determination of the said three-phase lines SS_BG and SL_2G is again sufficient for the calculation of the composition of the hydrate; the sole difference with the case of § 3 consists in this that a few corrections must be applied, which, however, can be calculated for the system sulphuretted hydrogen-water with sufficient accuracy from the data of the literature. The required corrections will be mentioned separately for each of the two three-phase lines.

5. *The threephase line SS_BG.*

Now the transformation on this three-phase line is not as in § 3 expressed by

$$AB_n \rightleftarrows A + nB - E_1,$$

$$(solid) \quad (gas) \quad (solid)$$
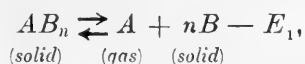
because the gas does not consist of the pure first component $(A = H_2S)$, but ice (solid B) has always some, though little, vapour tension. Hence a modification only occurs in the gas phase. When from the observed pressures P we now subtract the tension of ice of the same temperature, we find the values $P(corr)$, which accordingly denote the partial pressures of the sulphuretted hydrogen in the gas phase [1]. When we now determine $log\, P(corr)$ and the corresponding T^{-1} values, the graphical representation yields a curve which only little departs from a straight line. For this curve the following equation holds :

$$T\, \frac{dP(corr)}{dT} = \frac{Q_1}{RT}\, P(corr)$$

or integrated over a small range of temperature, where Q_1 may be considered as constant:

$$ln\, P(corr) = -\frac{Q_1}{RT} + C_1.$$

If the curve does not differ perceptibly from a straight line, this expression may be directly applied to the whole line and Q_1 can be calculated from the inclination.

If the curve has a perceptible curvature the value Q_1 can be calculated for the small range of temperature in question from every time two observations for temperatures that differ little (indices a and b) by the aid of

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[1] In this we, therefore, assume that the compound does not exist in gaseous state. If it occurs for a small amount in gaseous state, its influence will certainly remain within the errors of observation, the tension of water vapour being already small itself.

$$ ln\ P_a\ (corr) - ln\ P_b\ (corr) = -\frac{Q_1}{R}\ (T_a{}^{-1} - T_b{}^{-1}) $$

This value Q_1 is, therefore, the heat which would be required for transformation, if ice had no vapour tension, and agrees, therefore, in significance with the homonymous heat of § 3. It is the heat that we want for the calculation; it is a function of the temperature, but only a feeble one; the change of the heat of transformation with the temperature is namely expressed by the algebraic sum of the specific heats of hydrate, n molecules of ice, and one molecule of sulphuretted hydrogen at constant pressure (see § 3). If the law of KOPP is valid this sum of specific heats will be indicated by the difference between that of one molecule of solid H_2S and one molecule of gaseous H_2S (at constant pressure). As now the specific heat of solid H_2S amounts to about 10 [1]), that of gaseous H_2S to about 8.5, and the difference is therefore 1.5, it is clear that this correction for a range of temperature of about 20° to a heat effect of about 5000 calories (see later) constitutes a correction of about 6°/$_{00}$, which is negligible for our purpose.

Hence the above calculation gives us the heat of the transformation:

$$.\ \underset{(solid)}{H_2\ S\ .\ n\ H_2\ O} \rightleftarrows \underset{(gas)}{H_2\ S} + \underset{(solid)}{n\ H_2\ O} - E_1\ .\ \ .\ \ .\ \ .\ \ (5) $$
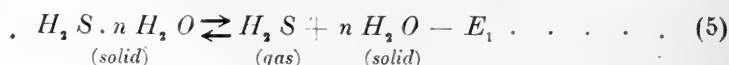
The change of energy E_1 may be found from Q_1 by deduction of the external work RT. (In the transformation evaporates one mol. of gas) [2]).

6.   *The three-phase line SL_2G.*

In the transformation $S \rightleftarrows L_2 + G - E_{SL_2G}$ an appreciable deviation from the corresponding case of § 3 occurs. For not only does sulphuretted hydrogen dissolve in the aqueous liquid, but water has also a definite not to be neglected vapour tension. The transformation at this equilibrium may be split up into:

$$ \underset{(solid)}{H_2\ S\ .\ n\ H_2\ O} \rightleftarrows \underset{(gas)}{H_2\ S} + \underset{(liquid)}{n\ H_2\ O} - E_2\ ,\ \ .\ \ .\ \ .\ \ .\ \ (6) $$

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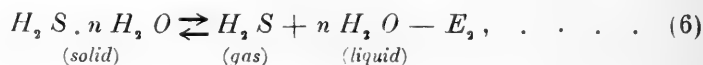
[1]) See NERNST. Theor. Chem. Gesetz von DULONG und PETIT.

[2]) In the same way as this has been done for the line hydrate-liquid-gas (see further on) the value of E_1 may also be calculated from $T\frac{dP}{dT} = \frac{Q}{V}$, in which V represents the volume gas formed by decomposition of one gramme molecule of hydrate (sulphuretted hydrogen + water vapour); then the heat Q must be corrected for the heat of sublimation of a small quantity of ice in order to find Q_1 and E_1 with it.

$$r\,H_2\,O \rightleftarrows r\,H_2\,O - r\,E_v \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\text{(liquid)} \qquad \text{(gas)}$$

and

$$s\,H_2\,S + \text{ much water } \rightleftarrows \text{ solution } + s\,E_0 \quad . \quad . \quad . \quad (8)$$

$$\text{(gas)}$$
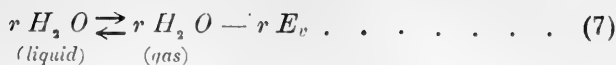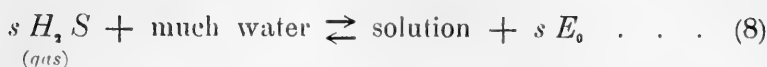
Then the total change of energy at the transformation becomes:

$$E_{SL_2G} = E_2 + r\,E_v - s\,E_0.$$

When we introduce the quantities of heat instead of the changes of energy, we get:

$$E_{SL_2G} + (1 + r - s)\,RT = E_2 + RT + r\,E_v + r\,RT - s\,E_0 - s\,RT$$

or

$$Q_{SL_2G} = Q_2 + r\,Q_v - s\,Q_0,$$

in which Q_2 represents the heat required for the calculation, and has a meaning analogous to that of the homonymous heat in § 3, Q_v indicates the heat of evaporation of one molecule of water, Q_0 the heat of solution of one mol. of H_2S.

$$(Q_v = 10780 - 11.3\,t^{1}),\ Q_0 = 4560^{2}))$$

When we now represent the number of molecules of H_2S that dissolves in one mol. of H_2O under three-phase pressure by q, the partial pressures of water and sulphuretted hydrogen by P_{H_2O} and P_{H_2S}, we have:

$$\frac{s}{n-r} = q \quad \text{ and } \quad \frac{r}{1-s} = \frac{P_{H_2O}}{P_{H_2S}} \ . \quad . \quad (9a \text{ and } b)$$

These equations may be transformed into:

$$s = q\,\frac{n - \dfrac{P_{H_2O}}{P_{H_2S}}}{1 - q\,\dfrac{P_{H_2O}}{P_{H_2S}}} \quad \text{ and } \quad r = \frac{1 - n\,q}{1 - q\,\dfrac{P_{H_2O}}{P_{H_2S}}}\,\frac{P_{H_2O}}{P_{H_2S}}.$$

or in approximation into:

$$s = n\,q \quad \text{ and } \quad r = (1 - n\,q)\,\frac{P_{H_2O}}{P_{H_2S}} \quad . \quad . \quad (10a \text{ and } b)$$

That this approximation is allowable, will appear from the data. (See the tables in the following paper).

Now follows from 10a and b:

$$1 + r - s = (1 - n\,q)\left(1 + \frac{P_{H_2O}}{P_{H_2S}}\right) \quad . \quad . \quad . \quad . \quad (11)$$

When we apply the equation of CLAPEYRON to the three-phase equilibrium in question, we find:

1) LANDOLT-BÖRNSTEIN-ROTH. Tables.

2) THOMSEN. Thermochem. Unters.

$$T\left(\frac{dP}{dT}\right)_{SL_2G} = \frac{Q_{SL_2G}}{\Delta V_{SL_2G}} = \frac{Q_2 + r\,Q_r - s\,Q_0}{(1 + r - s)\,RT}\,P_{SL_2G}\,, \qquad . \quad (12)$$

in which the volumes of solid and liquid are neglected by the side of gas, and BOYLE's law has been applied to the gas phase.

Transformation of (12) finally yields the required heat Q_2

$$\left(\frac{d\ln P}{dT} = -\frac{1}{T^2}\frac{d\ln P}{d\,T^{-1}}\right):$$

$$Q_2 = -r\,Q_r + s\,Q_0 - (1 + r - s)\,R\left(\frac{d\ln P}{d\,T^{-1}}\right)_{SL_2G} \qquad . \quad : \quad (13)$$

As now Q_r (heat of evaporation of one molecule of water) and Q_0 (heat of solution of one molecule H_2S) are known, r and s can be calculated from $10a$ and b (see also (11)), if an arbitrarily chosen value is substituted for n, Q_2 can be calculated if the temperatures are chosen close to each other, so that the differential quotient in (13) can be replaced by the quotient of differences [1]). Thus every time from two observations at temperatures differing little a value of Q_2 is found for that small range of temperature. This value Q_2, therefore, represents the heat of transformation on the three-phase line SL_2G, corrected for the phenomenon of solution and evaporation at the conversion. It is the heat belonging to the conversion:

$$H_2S\,.\,n\,H_2O \rightleftarrows H_2S + n\,H_2O - E_2 \qquad . \quad . \quad . \quad . \quad (6)$$
$$(solid) \qquad\qquad (gas) \qquad\quad (liquid)$$
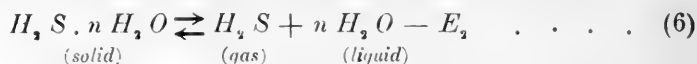
The heat Q_2 (and the change of energy E_2) will again be functions of the temperature. The algebraic sum of the specific heats is greater here than on the three-phase line SS_BG (§ 5); it may not be neglected. Hence the heat at transformation on SL_2G in the immediate neighbourhood of the quadruple point must be found by extrapolation. The correction required for this is, however, small enough to allow linear extrapolation, in other words to enable us to consider the specific heats as independent of the temperature.

Now the value of n follows simply from the equations (5) and (6) in a way analogous to that in § 3.

(*To be continued*).

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[1]) As r and s themselves represent corrections, a change of n brings about a modification in the correction which is already small. Whether 5 or 6 is chosen for n gives only a slight variation in the result of the calculations. We shall come back to this point later on.

Astronomy. — *"The distance-correction for the plates of the Harvard Map of the Sky"*. By Dr. H. Nort. (Communicated by Prof. J. C. Kapteyn).

(Communicated in the meeting of January 25, 1919).

It is a well-known fact that the limiting magnitude at the centre of a celestial photograph differs from that near its margin. If, e.g., the centre of a plate shows stars down to the photographic magnitude 11.0, this plate will at a certain distance from the centre show stars not fainter than, say, $10^m.8$. In the work of star-counts on photographic plates, therefore, it will be necessary to know for every plate the limiting magnitude as a function of the distance from its centre — or, as it is usually expressed: the *distance-correction* should be determined for each of the plates separately.

If we knew the photographic magnitude of a sufficiently large number of stars, then we should be able to determine directly the limiting magnitude for all parts of the plate and the distance-correction could easily be found. But, for a long time to come, photographic standards will be wanting and therefore, generally speaking, a direct determination of the distance-correction for plates covering a considerable part of the sky, is impossible. For such plates the only way is to use an indirect method, but this leads to difficulties, all of which have not yet been overcome. It is the aim of the present paper to deal with some of these difficulties.

In a previous investigation [1]) I have deduced the distance-correction for the *Harvard Map of the Sky*, a collection of 55 negatives on glass, on which Henie had made star-counts [2]). In this research I used the following method: firstly the variation of the star-density on each plate with the distance from the centre has been examined. It was tacitly assumed — and with regard to the following pages I want to emphasize this especially — that this density, without the so-called *"Bildwölbung"* and apart from local irregularities would have the same value all over the plate; in other words that a decrease

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[1]) H. Nort. The Harvard Map of the Sky and the Milky Way. Recherches astronomiques de l'Observatoire d'Utrecht, Vol. VII, 1917.

[2]) H. Henie. The Distribution of the Stars to the eleventh Magnitude. Lunds Universitets Årsskrift. N F. Afd. 2. Bd. 10. Nr. 1.

in the mean density from the centre towards the margin was only due to spherical aberration. Furthermore it was assumed that, for each plate, the mean density at equal distances from the centre had the same value; this means that the photographic plate was considered to have been focussed on its centre in a position perpendicular to the optical axis of the telescope.

Each plate of the Harvard Map, the film-area of which is 19×21 centi-metres, was divided into 7 concentric zones by circles having their centres at the centre of the plate and radii of 2, 4, 6, 8, 10 and 12 centi-metres respectively; each of the three outer zones consisted of four disconnected parts. Now, on each plate and for each of these seven zones the mean density was computed from Henie's counts [1] and so, for each plate, the density was found as a function of the distance from the centre. In order to eliminate as far as possible the individual peculiarities of the plates these mean densities of the zones have been divided by the mean density of the whole plate, thus giving the relative densities in the seven zones. These occur in Table VIII of the investigation mentioned above. [2]

In order to derive from this variation of the relative density the variation of the limiting magnitude, a relation between star-density and magnitude was to be assumed. Following the method used by Henie I expressed this relation by the following formula, which has been given by Charlier in his "Studies in Stellar Statistics" [3]

$$A\,(m) = \frac{N}{k\sqrt{2\pi}} \int_{-\infty}^{m} e^{-\frac{(m-m_0)^2}{2\,k^2}}\ dm$$

Here $A(m)$ is the number of stars covering a certain area of the sky and brighter than the magnitude m, while N, k, and m_0 are constants, which Charlier has determined by means of star-counts on the Carte du Ciel. For the computations, necessary to deduce with the above formula the distance-correction from the changes in the density, I wish to refer to my first paper. [4]

In determining the distance-correction I had to consider a complication which had not a priori been expected. There seemed no reason why the 55 plates taken with two equivalent instruments under similar conditions, should not, apart from local irregularities

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[1] l. c. table VII, p. 34.

[2] l. c. table VIII, p. 35.

[3] Lunds Universitets Årsskrift. N.F. Afd. 2. Bd. 8, Nr. 2, p. 32.

[4] l. c. p. 37 et seq,

show the same behaviour as to the results for the distance-correction. Table VIII, mentioned above, seems, however, to point to a different state of affairs. It shows not only that the relative density decreases from the centre to the margin, but also that this decrease is larger for plates with a large mean density than for those with a small one. This phenomenon makes it desirable that, in the further research, not all the plates should be treated in the same way; and so I divided them into groups, according to the mean density. Following HENIE I formed three groups; in the first group I took the 27 plates, which showed a mean density less than 20 stars per square degree, the second group was formed by 17 plates with a mean density between 20 and 35, while the 11 remaining plates, which had a mean density exceeding 35, formed the third group. The change in the relative density from the centre towards the margin being different for each of these three groups, they led to three different curves showing the variation of the distance-correction. These curves are shown in Fig. 1. The abscissae represent the distance from the

Fig. 1.

I   II   III
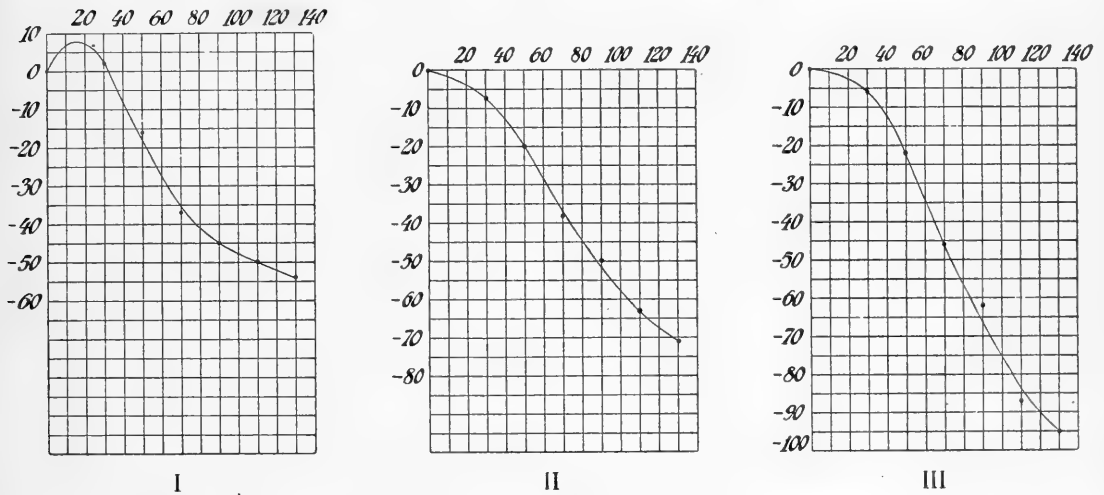
centre, in milli-metres; the ordinates give the difference between the limiting magnitude at this distance and that at the centre, expressed in hundredths of a magnitude.

There is a striking difference between the curves I and III, and it seemed important to investigate its cause. I have pointed out in my first paper that such a difference may be due to two causes. In the first place the colours of the stars might play a part. As said before, the decrease of the limiting magnitude towards the margin is an effect of spherical aberration, which, again, depends on the refractive index. Now, since the percentage of blue stars

increases as the Milky Way is approached, and since all the plates of group III, with a single exception, have their centres close to the Milky Way, it is not impossible that the difference between the curves I and III originates in the systematic behaviour of the star-colours. Since the colours of the majority of the fainter stars are still unknown, the influence, mentioned above, cannot be examined numerically.

Another cause of the difference between the two curves might be found in the influence of galactic condensation. Each plate of the Harvard Map of the sky covers about 900 square degrees of the sky, and it is obvious that such a large area will show the influence of galactic condensation and this in a higher degree where the centre of the plate is lying nearer to the galactic circle. In the course of my first investigation, Dr. P. J. VAN RHIJN of Groningen drew my attention to this fact; my objection then was that of the eight plates with centres near the galactic circle only three belong to group III. This, however, does not settle the question because the remaining five plates have not been included in group III for the only reason that they showed a mean density less than 35 stars per square degree. I, therefore, submitted the 11 plates of group III to a further investigation in order to get the distance-correction after elimination of a possible influence of the galactic condensation. For the 100 fields which have been counted on each plate we not only do know the star-density — the number of stars per square degree —, but also the galactic latitude; and this coordinate can easily be computed for the centre of the plate as well. From table V of Gron. Publ. N°. 27 [1]) I have, for every degree between $b = 0°$ and $b = 50°$, derived the value of $log. N$ for the visual magnitude 11.0 (this being the mean limiting magnitude of the Harvard plates) by graphical interpolation. With these logarithms the density of all the fields on a plate could easily be reduced to the galactic latitude of the centre. If, e.g. the density of a field is 20.7, its galactic latitude 14° and the galactic latitude of the centre 3°, then:

$$log\ 20.7 + [log N]_{3°} - [log\ N]_{14°}$$

represents the logarithm of the reduced density of that field. After the densities for each of the 11 plates had been reduced in this way to the galactic latitude of their centres, the distance-correction has been re-determined in the way described above. The result

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[1]) Dr. P. J. VAN RHIJN. On the Number of Stars of each Photographic Magnitude in Different Galactic Latitudes. Gron. Publ. N°. 27, p. 63.

showed, *that there exists still a pretty considerable difference between the plates of group I and those of group III with regard to their distance-corrections.* This is shown in the following table in which for the groups I, III (before reduction) and III (after reduction) the differences are given between the limiting magnitude at distances of 30, 50, ... 130 milli-metres from the centre and that at the centre. These numbers are expressed in hundredths of a magnitude.

	30	50	70	90	110	130
group I	+2	—16	—37	—44	—50	—54
group III (before red.)	—6	—22	—46	—62	—87	—95
group III (after red.)	—6	—19	—40	—52	—72	—79

From the fact that there remains a difference [1]) between I and III after they have been corrected for the influence of galactic conden-sation it follows that this difference must originate in the colours of the stars depending on their position with respect to the Milky Way. If this is the true cause, it would be better not to divide the plates into three groups according to their mean density, but into two groups according to the galactic latitude of their centres. We may, then, expect the plates of the first group (those outside the Milky Way) to give a distance-correction showing the characteristic properties of curve I in Fig. 1. The new curve for this group would probably show a slower decline than the old one, since now this group no longer contains plates whose centres have a small galactic latitude. The new second group, which now would contain only plates with small galactic latitude of the centres might be expected to yield a curve almost identical with curve III of Fig. 1. The results of the new classification proved to agree with what had been expected. The new group I contains 34 plates, whose centres have a galactic latitude $> 20°$; the remaining 21 plates form the new group II. Similar to curve I of Fig. 1 the new curve, showing the variation of the limiting magnitude for the plates of the new group I, has a pronounced maximum; but while the old curve went down as far as $- 54$, the new one only descends to $- 48$. The following table gives for the old and the new group I the differ-ences found when the limiting magnitude at the centre is subtracted from that at distances of 30, 50 .... 130 milli-metres from the centre

	30	50	70	90	110	130
group I (old)	+ 2	— 16	— 37	— 44	— 50	— 54
group I (new)	+ 3	— 13	— 32	— 39	— 46	— 48

[1]) Probably, this difference would still increase if we corrected the densities of the plates of group I for the galactic latitude of the centre. In this group, too, a few plates occur whose centres have a small galactic latitude.

while the following table gives these differences for the plates of the old group III and the new group II

	30	50	70	90	110	130
group III (old)	— 6	— 22	— 46	— 62	— 87	— 95
group II (new)	— 10	— 25	— 48	— 62	— 83	— 96

In this new classification neither the plates of the first group nor those of the second group have been corrected for galactic condensation. This correction, if applied, would have $n\dot{o}$ influence on the distance-correction for the first group; for the second group it would, of course, lead to numbers not materially differing from the numbers given in the third row of the first table on page 1217. Therefore the distance-correction, freed from the influence of galactic condensation may be considered to be as follows.

	30	50	70	90	110	130
group I (new)	+ 3	— 13	— 32	— 39	— 46	— 48
group II (new)	— 6	— 19	— 40	— 52	— 72	— 79

The results of this investigation may be summarized in the following conclusions:

1. The plates of the Harvard Map of the Sky, with regard to the decrease of the limiting magnitude from the centre towards the margin should be arranged into two groups. As the criterion for this classification the galactic latitude of the centres of the plates and not their mean density must be chosen.

2. On the plates which have their centres *outside* the Milky Way the limiting magnitude increases to a distance of about 16 millimetres from the centre and decreases from there to the margin. On the plates which have their centres *in* the Milky Way the limiting magnitude is continually decreasing from the centre and this decrease exceeds that for the plates outside the Milky Way.

3. The effects, mentioned sub 1 and 2 probably result from the so-called KAPTEYN-phenomenon.

Gouda, January 1919.

Microbiology. — *"Oidium lactis, the milkmould, and a simple method to obtain pure cultures of anaërobes by means of it."* By Prof. BEIJERINCK.

The many methods recommended for the pure culture of anaërobes, — whose multitude proves that none of them quite satisfies the investigators, —. may be distinguished in chemical and biological. As to the former, of which Novy's exsiccator method is certainly the best, everything has been tried. This cannot be said of the biological methods based on the use of living organisms in particular aërobic microbes for the removing of the oxygen. For myself only after using the milkmould to that end I have obtained results worth fixing once more the attention on it.

Some chief points from the life history of *Oidium lactis* important for experiments with this species may precede; a complete description is not necessary here.

Properties of the milkmould.

The milkmould possesses a number of properties which render it very fit for experiments in relation to respiration, nutrition, growth and symbiosis. It unites the character of the moulds to that of the yeasts, in particular with regard to the growth in and upon the substrate which takes place without being accompanied by fermentation, as also without the formation of conidia which currents of air might spread. Within the substrate the long-celled mycelium is found, on the surface the chains of conidia which, even when extending free in the air, cohere and never contaminate the environment as moulds may do.

It is easily obtained. A rich growth results when market milk is left a few days in an open glass in a warm room; the milk then always covers with an *Oidium* film. Lactic acid ferments also develop and by their production of acid further the growth of *Oidium*, whilst they themselves are favoured in their development by *Oidium*, because it oxidises the lactic acid to carbonic acid and

water. In garden soil *Oidium* is generally spread as may be shown by inoculating feebly acidified malt infusion with soil and keeping it at 25° to 30° C. The film which finally covers the liquid contains besides *Mycoderma*, always *Oidium*. Pressed yeast, long whey, sour milk, cheese, the output waters of distilleries and all kinds of acid sewage, are inhabited by *Oidium*. Natural habitats are furthermore the sap flow of many trees caused by *Cossus ligniperda* and allies.

For pure culture acidified malt infusion- or broth-glycerin plates are recommendable. The acid serves to exclude the hay bacteria which have a great disposition to grow in symbiosis with *Oidium* in neutral environment.

The transfers for the collection are kept on malt-agar, but they change thereby in a few months into a tough, leathery mycelium, almost exclusively consisting of long mycelial threads difficult to separate and evenly to mix with the nutriment. To obtain normal material in this case a new isolation from milk or soil is necessary, for the change is an hereditary non-reversible mutation.

Under favourable feeding conditions the growth is remarkably rapid and the respiration and oxygen absorption go parallel with it. This intensity exceeds by far that of the ordinary moulds of the genera *Penicillium* and *Aspergillus*, whilst it equals that of *Mucor*. This holds, however, only good with regard to easily assimilable substances; less decomposable matter such as pectine, cellulose and chitine are not attacked by *Oidium*. Gelatin and agar are neither assimilated. Fermentation phenomena, joined with the evolution of gas, are as said also wanting. Hence, *Oidium* never forms rents or holes in the solid substrata wherein it is cultivated, not even in presence of glucose. This is one of the reasons why it is so well adapted to the culture experiments with the anaërobes to be discussed below.

The products of metabolism are chiefly or only water and carbonic acid; volatile or non-volatile substances noxious to other organisms are not produced.

In regard to carbon-food *Oidium* exhibits a great specialisation. Most hexoses, in particular glucose, levulose and mannose, are readily assimilated and oxidised. Likewise aethylalcohol. Glycerin, too, is a very good carbon source. On the other hand, starch, raffinose, maltose, cane sugar, mannite and all similar substances, are in no way assimilated. Enzymes, as diastase, maltoglucase, invertase, lactase, are hence completely absent. Glucoside enzymes could neither be found. By the absence of these enzymes, *Oidium*, which so easily reacts on the hexoses, is especially fit as a reagent on these enzymes in case they are to be detected in parts

of higher plants or as products of secretion of other microbes; here the auxanographic method may advantageously be applied.

Fats are however split up by *Oidium*, by means of the exoenzyme lipase, active outside the cells. Hence, in presence of fats growth of *Oidium* may be expected at the expense of glycerin and this explains the general occurrence of *Oidium* as well in milk and butter as in other fat-containing materials. For the preparation of lipase the milkmould can afford a good starting material.

As to the nitrogen food *Oidium* resembles the ordinary yeast species and is in this respect rather many-sided. With exception of nitrates and nitrites, and unchanged albuminous substances, the ordinary nitrogen compounds are easily assimilated in presence of good carbon food such as glucose and glycerin. This is in particular true for ammonium salts and urea. Peptones and the higher ammino acids, if alone, are not or very slowly assimilated, but in presence of a good carbon source they may serve as a very good nitrogen food, so that the complete nutrition of *Oidium* in presence of these substances should be called dualistic. Consequently broth bouillon is for *Oidium* an insufficient food and on a broth-agar plate it develops but poorly. This changes however by adding a good carbon source. If this is done locally on a broth-agar plate there results an auxa-nogram in the diffusion circle of the related matter, which proves at the same time that the other elements required for the growth of *Oidium*, as potassium, magnesium and phosphor, are present in sufficient quantity in the broth. As these elements accumulate in the young cells, either as the same chemical compound found in the substrate or not, such experiments are apt to demonstrate the absorption phenomenon formerly described by me. It is also easy in reversing the experiment, that is by feeding with carbo-hydrates, to find with the microscope by means of iodine, gly-cogen accumulated in the so large *Oidium* cells and its disappearing in the auxanograms of nitrogen food, such as ammonium salts or urea, as soon as the carbon food in the substrate is wholly assimilated.

A feebly acid reaction of the medium furthers the growth of *Oidium*, and organic acids, for example acetic and lactic acid, may disappear by oxidation. Other acids as molybdenic and tungstic acid are in good media, such as glucose-broth-agar, reduced by *Oidium* to the well-known blue oxides, which gives rise to beautiful colour experiments. In neutral solutions the salts of these acids are however not affected so that this is a case of reduction in an acid medium. The ordinary alcohol yeasts behave likewise.

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Use of the milkmould for the pure culture of anaërobes.

In nature the withdrawing of oxygen from the environment, which is required for the development of anaërobes, is usually caused by aërobic microbes.

They not only absorb the last traces of oxygen from the surroundings but even produce reducing substances in it. In the laboratory this may be imitated by adding to a culture medium containing in small number germs of the anaërobe to be examined, a great number of germs of an appropriate aërobic microbe. How such experiments have hitherto been carried out [1]) may be illustrated by a definite example namely the cultivation of the spore-forming aërobes of the albumin putrefaction; then I will describe the modified method.

A crude culture of putrefaction bacteria is obtained thus. A stoppered bottle is quite filled with a watery infusion of albuminous matter, infected with garden soil and boiled to kill all non-sporogenous microbes. Placed in the incubator the mass soon passes into stinking putrefaction, characteristic by the presence of mercaptans produced by the spore-forming anaërobes. Now to ordinary broth-gelatin or broth-agar an abundant quantity of some intensively growing aërobic bacterium, such as *B. fluorescens* or *B. prodigiosum* is added, together with a little of the to 90° or 100° C. heated material containing the spores of the putrefaction microbes. After solidification in a test tube the aërobes near the bottom will soon absorb the last traces of oxygen and being unable to grow there, not give rise to liquefaction of the gelatin; but they will retain the oxygen penetrating from above and develop strongly in the surface of the gelatin. In the lower part of the tube the spores of the putrefaction bacteria can now germinate and if gelatin is used there will soon appear the large liquefying colonies of the so remarkable *Bacillus septicus*, together with the non-liquefying putrefiers, for the greater part recognisable by the flocculent structure of their colonies, a character related to their sensitiveness to extension and contraction of the substratum wherein they grow, quite as by *B. Zopfii*. For the microscopical examination this method undoubtedly affords good material, but it is hardly possible to reach the single anaërobic colonies without touching others. To this end it is necessary to remove the culture gelatin from the tube by heating it in the flame so that only the outer side of the gelatin melts and the contents may be thrown

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[1]) E. Macé, Traité pratique de Bactériologie, 6e Ed. T. 1, pag. 305, Paris 1912. Besson, Technique microbiologique et sérothérapique, 6e Ed., pag. 102, Paris 1914.

out as a whole. One may also with a file make an incision in the glass wall in the neighbourhood of favourably situated colonies. But it is clear that there is much chance that thereby also different colonies intermix so that of a pure culture of anaërobes in the usual sense of the word there is no question in such experiments. For examination with the microscope and for studying the appearance of the colonies the method is useful, but for the culture of pure species it is worthless.

Every good method for pure culture of aërobes and still more of anaërobes should answer the following requirements: the colonies must be situated quite free and at due distances from each other on the surface of the solid plates, they must furthermore be readily attainable with the platinum wire. These requirements can only be satisfied by cultivation in ordinary glass boxes or Petri dishes, which may take place in the laboratory by means of the exsiccator method of Novy (see MACÉ, l.c.).

After this method, — the best of the chemical ones, — ordinary culture boxes are placed in an exsiccator filled with pure hydrogen and moreover containing some oxygen-removing substance, such as ferro-ferrocyan or alkaline pyrogallol. But this method also has its drawbacks. It is namely impossible quite to prevent the deposition of vapour at the glass covers, so that drops of water falling down come on the plates; this makes the colonies intermix and spoils the experiment. It is, besides, hardly possible distinctly to see the state of development of the colonies in the closed exsiccator, which may lead to it being opened too early and oblige the experimenter to begin anew. This is very troublesome considering the complication of the experiment.

The *Oidium* method has none of these disadvantages, and if well-managed, produces colonies of the anaërobes situated quite free on the surface of the plates and easily reached with the wire.

The principle of the method is the placing one over the other of two culture plates, separated by a relatively small space of air. One of the plates contains the aërobic microbe which is to absorb the oxygen, while on the surface of the other the anaërobe is to grow. Here, also, I select a definite example for illustration, namely the strictly anaërobic bacilli of the butyric-acid and the butyl-alcoholic fermentations; they have corresponding nutrition conditions and may be isolated in the same way. They are spore-producers, thriving best in malt infusion where they cause strong fermentations accompanied with production of hydrogen and carbonic acid. A crude butyric-acid fermentation is prepared as follows. Wheat- or rye-flour, or better a pap of potatoes infected with soil, is mixed in a glass beaker

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with water to which is added some calcium-carbonate, then heated for a few seconds to 90° or 100° C. Kept at 30° to 40° C. there usually results after two days a strong butyric-acid fermentation in which occur various butyric-acid bacteria which are then to be isolated.

For the preparation of a crude butyl-alcoholic fermentation crushed corn[1]) of *Hordeum vulgare nudum* may be used; a pap of potatoes infected with soil and heated not higher than 80° to 85° C. will also do; addition of chalk is not necessary, the butyl bacteria producing no acid. Of course the spores of butyric-acid ferments are still present in such preparations and the surprising fact that by application of the said temperature no butyric-acid but a butylic fermentation ensues, should probably be attributed to the injurious action of the butyl alcohol on the butyric-acid ferments.

The pure culture is effected as follows.

Malt-infusion agar with 5° to 10° glucose is liquefied and after cooling to near solidification and addition of a great quantity of *Oidium lactis* is plated (Op) in a large glass dish (Gs_1). At a temperature of 25° to 28° C. the whole surface of the plate is already after 24 hours covered with a thick snow-white film of conidia and the interior of the agar is wholly interwoven with mycelium, which causes a considerable absorption of oxygen.

A second malt-infusion-agar plate (Ka) without *Oidium* is now prepared in a glass dish (Gs_2), much smaller than Gs_1. The space between Gs_1 and Gs_2 must be large enough Gs_2 to be caught with the fingers. On its surface a little of the material containing the anaërobes, that is of the crude butyric-acid or butyl-alcoholic fermentations, diluted with sterile water, is spread. Now the lid of the smaller dish (Gs_2) is removed and the plate pressed on the *Oidium* plate the agar side (Ka) upward as shown in the figure.

For the escaping of the air from Lr a little hole g is bored in the glass wall of Gs_2 and closed with a droplet of paraffin introduced with a heated glassrod. At 28° to 30° C. the air in Lr, which space can be relatively small, will soon be free from oxygen and the anaërobes on Ka can begin to grow. To further the absorption of oxygen from the agar Ka in Gs_2, *Oidium* may also be added to it, but then a thin layer of malt agar without *Oidium* should be poured on the surface of Ka to obtain a germ-free surface for the sowing of the anaërobes. *Oidium* being strictly aërobic the mycelia do not perceptibly grow through this protecting layer.

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[1]) Fermentation et ferments butyliques. Archives Néerlandaises I. 39. Pag. 1. Bactéries actives dans le voisinage du lin. Ibid. Sér. 2. I. 9. p. 418. 1904.

If the glass dishes have good dimensions and the space Lr is not too small, one can sideways look through the glass wall and follow
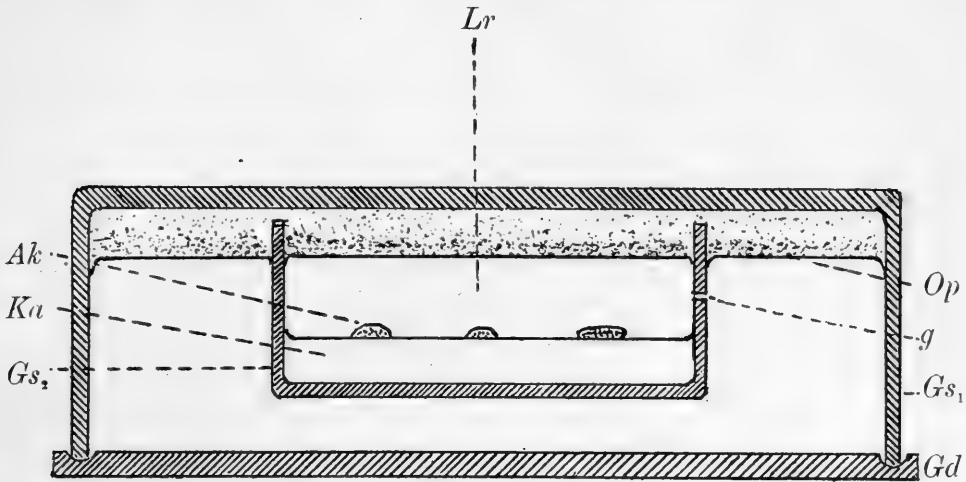
Cultivation of anaërobes by means of *Oidium lactis*. Gs_1 large glass dish with the oxygen-absorbing *Oidium* plate Op. Gs_2 smaller dish with the culture plate Ka whereon the anaërobic colonies Ak grow. Lr space between the plates. At g the hole in the glass wall of Gs_2 for the escape of the air from Lr, which is afterwards closed with paraffin. Gd glass lid of the large dish Gs_1. The higher temperature is at the side of Gd.

the development of the anaërobic colonies on Ak. So it is easy to decide when the moment for further observation has come without it being necessary to remove plate Ka from the *Oidium* plate Op, and thus prevent too early opening.

When it is time to open, liquefied malt agar must be at hand to be poured out over the *Oidium* plate, especially in the groove formed by Gs_2, as soon as plate Ka is to be restored to its place. The fresh food causes new oxygen absorption by *Oidium* and the growth of the anaërobes can go on.

For the success of the experiment it is essential to mind the following. The placing in the incubator should be managed in such a way that the *Oidium* layer Op comes in the cooler, and the cover Gd as also plate Ka in the warmer part. The vapour in Lr will then condense in Op and not on the surface of Ka. In the reversed position Ka will become moist, the colonies intermingle and the experiment fails. Hence the figure is represented in such a position that the colder air is above, the warmer below, as is the actual state in an incubator with bottom-heat. How simple all this may appear, in the execution it will be found necessary to pay special attention to it.

In this way it is possible from the ordinary crude butyric-acid fermentations, obtained as described above, to separate three distinctly different *Amylobacter* species, two of which I described already before (Proceedings Vol. 12, Pag. 973, 1903) under the names *A. (Granulobacter) saccharobutyricum* and *A. (G.) pectinovorum*, while from the butyl-alcoholic fermentations two species were isolated, one of which produces large slimy colonies and was described as *A. (Gr.) butylicum* (Archives Néerlandaises, 1re Série, T. 29, Pag. 2), whereas the other, which secretes no slime, has not yet been investigated. The colonies of all these species colour dark blue with iodine like starch, the staves and clostridia containing a great quantity of granulose.

The butyric-acid and butyl-alcoholic fermentations acquired in other ways than the above mentioned have not yet been examined thoroughly.

As the anaërobic *Sarcina ventriculi* likewise develops very well on malt-infusion agar at 30° tot 37° C. (Proceedings 28 April 1911, Pag. 1412), this species may be isolated just in the same way as the above.

As regards the spore-producing bacteria of the real protein putre-faction the *Oidium*-plate may be prepared just as in the experiment described, only for the cultivation of the anaërobes themselves in Gs_2 it is better to make use of broth agar with 0.5 or 1 °/$_0$ common salt, either with addition of 2 °/$_0$ glucose or not. In this case, too, nutrition with carbohydrates gives in some species rise to production of granulose, in others not.

Another anaërobe isolated by the *Oidium*-method is *Bacillus acidi urici* (Proceedings 23 April 1909, Pag. 990), which ferments uric acid to carbonic acid, ammonium acetate and ammonium carbonate This species also develops best on broth agar at 30° to 35° C.

For beginners it must be noted that on plate *Ka* the facultative anaërobes, such as *Bacterium aërogenes* and *B. coli*, develop quite well, as may be proved by streaking off all the colonies *Ak* on aërobic plates on which the anaërobes only do not grow. This is in accordance with the fact that at the starting of the experiment some oxygen is present in *Lr* sufficient for the very small oxygen want of the facultative, better called temporary anaërobes.

Anatomy. — *"The sympathetic innervation of the cross-striated muscle fibres of vertebrates."* By Prof. J. Boeke and Dr. J. G. Dusser de Barenne.

Some years ago one of us, partly in these proceedings and in the transactions of this Academy [1]), published a number of observations, which tended to show that on the cross-striated muscle fibres of reptiles, birds and mammals there existed, beside the usual motor endplates, still a second set of hypolemmal nervous endorgans, very fine and delicate, which are seen in Bielschowsky-preparations as very small neurofibrillar end-rings and small end-nets, lying on the surface of the muscle-fibres at the end of fine non-medullated nerve-filaments. These so-called "accessory" nerve-endings lie hypolemmally on the muscle-fibres embedded in the granular sarcoplasm of the fibre, and in some cases are found in the same layer of granular protoplasm which surrounds also the terminal ramifications of the common motor end-organ; in other cases they are found as separate endings, lying embedded in a distinct layer of nucleated sarcoplasm independent of the motor sole, but, as far as could be made out, they always appear as hypolemmal structures. The non-medullated nerves that have these end-organs attached to their terminal nerve-ramifications, are seen running in bundles between the muscle-fibres, remain amyelinic throughout their whole course, and seem to form a distinct system of nerve-fibres, independent of the motor and sensible nerves. These observations, and especially the amyelinic structure of these nerve-fibres gave room for the supposition, that this so-called "accessory innervation" (Boeke, 1909) is of a sympathetic nature, and in this way the conclusion was drawn (Boeke, 1909, 1911) that the cross-striated muscle-fibres (the end-organs, mentioned above, were found in the muscles of the tongue, the eye, the iris, the back, the m. pectoralis, in the intercostal muscles, and afterwards Aoyagi found the same structures in the muscle of the diaphragm) are not only innervated by the spinal nerves, but also by the sympathetic system. The function of this sympathetic inner-

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[1]) J. Boeke, Studiën zur Nervenregeneration I and II. Verhandelingen K. A. W. Second series. Vol. 18 and 19.

vation might be of a tonic or of a trophic nature. This question however is to be answered by means of physiological experiments, and the investigation of it therefore must be left to practised physiologists, and need not to be discussed in this paper.

The sympathetic nature of these "accessory" fibres could be shown afterwards by cutting the eye-muscle-nerves (trochlearis, oculomotorius) directly after they have left the mid-brain, which caused the sensible and motor nerve-fibres to degenerate. The accessory non-medullated nerve-fibres however and their end-organs on the muscle-fibres remained unaltered (BOEKE, 1911, 1916), which could only be explained by admitting, that they are transferred to the eye-muscle nerves by way of the sympathetic branch, which reaches the orbita along the arteria opthalmica from the plexus caroticus, so that they were not dissected when the eye-muscle nerves were cut directly behind their place of origin from the brain-stem.

Experiments, in which a series of spinal nerve-roots of the cat were cut, made in collaboration with Prof. MAGNUS, however did not give clear and unquestionable results, which perhaps may find its explanation in the fact, that the elements of the sympathetic nervous system generally take the stain far less readily than the other nervous elements. A negative result of a staining reaction is therefore in no case evincing for the non-existence of these sympathetic elements. Afterwards similar experiments have been executed with better results, and Dr. AGDUHR, who has a communication on this subject appearing in this number of the Proceedings, obtained the same definite and positive results with the muscles of the extremities as those, which we are going to describe for the intercostal musculature.

The experiment, the result of which we are going to describe here, was executed by one of us (D. DE B.) in the following manner:

In a cat were extirpated at the right side of the medulla spinalis inside the dura mater a series of 4 consecutive ganglia spinalia with simultaneous section of the corresponding posterior and anterior roots. This was done on the 15th of February. The wound healed per primam, the animal remained healthy. A month afterwards (15th of March) the animal was killed by chloroform, and the blood-vessels were cleaned thoroughly by rinsing them with RINGER's fluid. After that the thoracic wall was rinsed with a neutralised solution of formalin (12 %), and preserved in formalin 12%, alcohol 60 %. The autopsy showed that the posterior and anterior roots of thoracalis VI, VII, VIII and IX with the corresponding ganglia spinalia were cut through. The most reliable results therefore were to be expected

J. BOEKE and J. G. DUSSER DE BARENNE: "The sympathetic inner-
vation of the cross-striated muscle fibres of vertebrates".
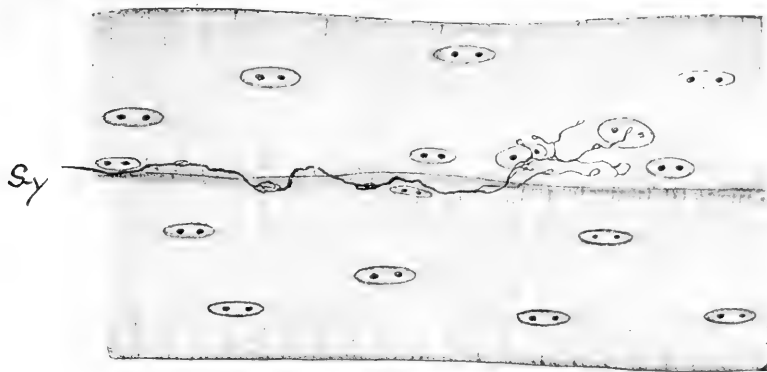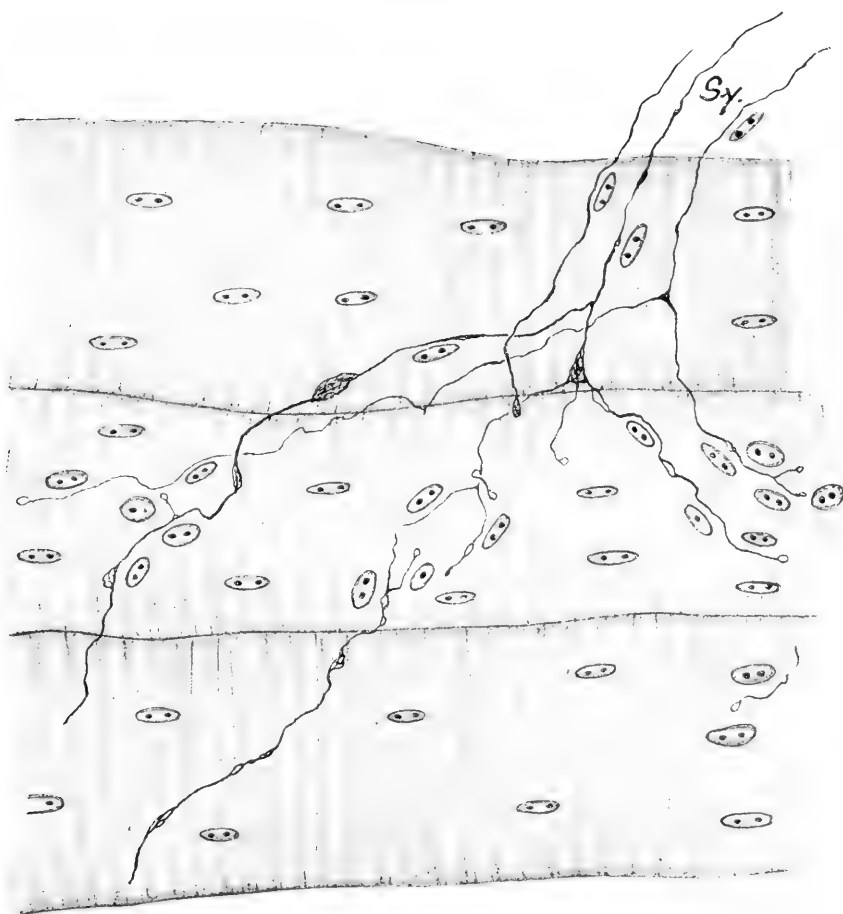
Fig. 1.

Fig. 2.

DESCRIPTION OF FIGURES.

Fig. 1 en 2. Muscle-fibres from the musc. intercost. of the 7th intercostal
space, with non-medullated nerve-fibres and end-organs, which remained intact
after the dissection of the roots and exstirpation of the ganglia spinalia of the
VI, VII, VIII and IX intercostal nerve in the cat. Magn. 1800 diameters.
sy = sympathetic nerve-fibres.

from the microscopical examination of the intercostal muscles of the seventh intercostal space. Pieces of these muscles were cut out, stained after the method of BIELSCHOWSKY and afterwards cut into serial sections of 10μ—30μ and studied.

The staining reaction gave excellent results, even the finest neurofibrillar threads being distinctly visible in the sections, and from the examination of the serial sections the following conclusions may be drawn: the axis-cylinders and the myelinic sheaths of the motor and sensory nerve-fibres were entirely degenerated and had disappeared. Only the neurilemma and the nuclei of SCHWANN remained visible in the form of the curious protoplasmic bands of BÜNGNER, so characteristic for degenerated nerve-fibres; of the original motor end-plates no trace was to be found, only the thickened layers of multinucleated granular sarcoplasm (soles) were to be seen, indicating the place of the original motor end-plates, the neurofibrillar structure itself having entirely disappeared. So the motor and sensory nervous elements of the intercostal muscle-fibres of the 7th intercostal space were absolutely degenerated. Not a single medullated nerve-fibre was left intact. But then there appeared in the sections between the muscle-fibres thin bundles of fine non-medullated nerve-fibres, often composed only of two or three threads (fig. 1 and 2), and when we follow these fibres under the microscope until the point where they seem to end, they appear to be connected with the muscle-fibres by means of very small and delicate end-organs, end-rings or loops or small endnets (fig. 1, 2). Not only at the end of the nerve-fibres, but also here and there in their course, often small side-branches are given off, which come into connection with the muscular fibre across which the nerve-fibre is running, by means of the same small endrings. A look at fig. 2 gives a better idea of the structure and form of these different endrings than a long and detailed description. Fig. 1 teaches us, that besides the small endrings and endnets more complexly built structures occur also, but even these are always finer and more delicately built than are the common motor end-organs. This case besides shows us the terminal ramifications of the neurofibrillar structure lying embedded in a layer of granular sarcoplasm which contains a number of nuclei (3). This seems to indicate, that the endorgan in question has a hypolemmal position.

In fine, the form of these end-organs and their neurofibrillar structure are exactly identical with that of the terminal ramifications and end-organs of the non-medullated nerve-fibres, which remained intact in the eye-muscles after the stem of the eye-muscle nerves had been cut through (BOEKE, 1911, 1916), and we may

reckon them to belong to the same class of the so-called "accessory" innervation apparatus of the cross-striated muscle-fibres.

These nerve-fibres and their endorgans on the voluntary muscle-fibres, described above, cannot well be otherwise than of a *sympathetic nature*. Non-medullated nerve-fibres in general take a longer time to degenerate after section of the nerve than do the medullated fibres and their end-organs. Whilst as a rule 3 or 4 days after dissection of the nerves all the motor nerve-endorgans on the muscle fibres have disappeared, it is possible to find here and there in the sections seemingly intact non-medullated nerve fibres as long as 14 days after dissection of the nerves. But when we give the nerve-fibres, as was done in the experiment described above, a month to degenerate in, before the animal is killed, we are sure to find *all* the *dissected* nerve-fibres, medullated and non-medullated degenerated. So when, after the lapse of a month, we kill the animal, and when we then find in the sections intact nerve-fibres, clearly and sharply outlined, which take the neurofibrillar stain readily, and are found ending in beautifully-stained regular endrings and endnets, we are justified to draw the conclusion, that these nerve-fibres were not cut through when the nerves were dissected. It follows from the description of the experiment, that these intact nerve-fibres must be fibres which enter the nerves after the ganglion spinale has been passed, and whose trophic centre, the ganglioncell, lies outside the medulla spinalis and outside the ganglion spinale, viz. sympathetic nerve-fibres, derived from ganglion-cells lying in the ganglia of the sympathetic chain.

So our experiment has given convincing evidence for the exactness of the conclusion, drawn by one of us (Boeke, 1911, 1916) from his former observations.

It is proved by the results of our experiment, at least for the muscles of the trunk, not only that the accessory fibres and their end-organs belong to the sympathetic system, but also, that they are sympathetic elements with a c e n t r i f u g a l, e f f e r e n t trans-mission of nerve impulses.

In the communication by Dr. Agduhr, appearing in this same number of the Proceedings, it will be shown, that the identical con-clusion may be drawn for the muscles of the extremities.

Leiden,
Utrecht, January 1919.

Anatomie. — *"Are the cross-striated muscle fibres of the extremities also innervated sympathetically?"* By Dr. Erik Agduhr. (Communicated by Prof. J. Boeke).

(Communicated in the meeting of 25 Jan. 1918).

In the Anatomischer Anzeiger, Bd. 44 Boeke [1]) gives an account of how he has shown morphologically that the cross-striated muscle fibres in the m. obliquus oculi superior of the cat are innervated not only by cerebral but also by sympathetic nerves. He describes how he made a section of the n. trochlearis near the basis of the brain and let the animal live till the nerve fibres that had been cut off, peripherically of the place where the sections were made, had undergone degeneration that could be proved morphologically. He also found in Bielschowsky-impregnated sections from the m. obliquus oculi of the animal that the medullated nerves had undergone degeneration. By the side of these degenerated cerebral nerves Boeke found, however, intact nerves free from medullary sheaths, which ended in terminal loops in or on the muscle fibres.

Boeke was able to show that the terminal loops had a hypo-lemmal position and on account of this he is of the opinion, that the intact nerves are of an efferent nature. The position on the muscle fibres of the terminal loops of these nerves was partly inside and partly outside the region of a motor plate. In this way Boeke had of course put forward evidence of the innervation of the cross-striated muscle fibres by sympathetic nerves as well.

This morphological evidence of Boeke has caused me to investigate the occurrence of such nerves in the musculature of the extremities. It is well known, that the inner orbital muscles are exceedingly well supplied with nerves, and the possibility that only these and no other cross-striated muscles are innervated sympathetically is of course quite a reasonable one, even though it is not obvious. During my investigations on the plurisegmental innervation of the separate cross-striated muscle fibres I had in addition observed in the muscles of the extremity a number of terminal organs of nerves, which I could not interpret with certainty. I had also noticed a

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[1]) Boeke, J. Die doppelte (motorische und sympathische) efferente Innervation der quergestreiften Muskelfasern. Anat. Anz., Bd. 44, 1913.

number of nerve endings that reminded me of those described by BOEKE as "accessory". This state of affairs compelled me, before continuing the segmental investigations mentioned above, to attempt to answer the question: "Are the cross-striated muscle fibres of the extremities also innervated sympathetically?", and in addition, in case the question could be answered positively, to study in somewhat more detail the terminal organs of these nerves in the extremity-musculature.

There were really two ways in which I could set about answering this question, I could either bring all the spinal nerves in the extremities into degeneration, taking care that all the sympathetic nerves to the extremities remained intact, or else I could bring the sympathetic nerves into degeneration while the spinal ones were left intact. I chose both methods, so that I might possibly arrive at results that agreed with each other and that were therefore so much more certain.

In order to bring into degeneration the sympathetic nerves of the extremity the ganglion stellatum of one side was extirpated in two cats. The cats were kept alive for a few days (four and six respectively) after the operation. In sections of *B*-impregnated extremity-muscles from the animal in which degeneration had proceeded farthest I was successful in showing the remains of degenerated nerves that were without medullary sheaths. I shall give a more detailed account of this part of the investigation in a more complete description. I shall enter here into somewhat more detail about the other part, i.e. the bringing into degeneration of the spinal nerves, taking care that the sympathetic ones remained intact.

I cut off the last four cervical and the first two thoracal nerves in the foramina intervertebralia of several cats. The sections were made between the ganglion spinale and the place where the ramus communicans albus goes off. The wounds were sutured and began to heal per primam intent. The animals were killed after different periods of time varying from five to ten days after the operation. The animal from which were taken the preparations, on which the following description is based, was killed five days after the operation. On account of the operations that had been carried out it could thus be assumed that after a sufficient length of time degeneration would occur — peripherically of the place of the section — in the spinal nerve fibres of the segmental nerves that had been cut off and also in their pre-ganglionar sympathetic nerves. On the other hand there was reason to expect that the post-ganglionar sympathetic nerves were kept intact. The shortest of the periods of degeneration

taken should be sufficient to show degeneration (peripherically of the place where the cut was made) in Ag — impregnated preparations of the nerve fibres that had been cut off. TELLO[1]) gives further details about the time of the appearance of degeneration that can be shown morphologically in the nerves peripherically of the place of the section.

The plexus brachialis of the cat is generally formed by the ventral branches of the first thoracic nerve (I have sometimes, however, observed a fine branch from the second thoracic nerve) and the last three cervical nerves. As is shown above, one segmental nerve cranially and one caudally of those that generally form the plexus had thus been caused to degenerate. This was done to ensure complete certainty that, even if some branch might possibly come from these contiguous nerves to the anterior extremities, all the spinal nerves there would have undergone degeneration. After the animal had been killed, the results of the operation were carefully verified, and they were found to be good. The animal in question had no branch from the second thoracal nerve to the plexus brachialis. After the blood had been removed by injecting physiological solution of common salt from the heart, the anterior extremity on the side where the animal had undergone the operation was fixed by injecting a twenty per cent solution of formaldehyd from the a. axillaris. The extremity was kept for some time in formalin. The mm. interossei were impregnated according to my modifications[2]) of BIELSCHOWSKY's method of silver impregnation.

It was clear from sections of the impregnated muscles that all the myelinized nerves, both the motor ones and the sensory ones, had undergone degeneration. On the other hand I found quite a number of intact non-medullated nerves. These intact nerves were found in the preparations partly together with bundles of degenerated spinal nerves and partly along vessels. I was able to follow a large number of the intact non-medullated nerves out to their terminal organs. These terminal organs were situated partly on ordinary cross-striated muscle fibres and partly on muscle fibres in muscle-spindles. I shall give a more detailed account of the sympathetic terminal organs in muscle spindles in a later and more complete

[1]) TELLO, F. Dégénération et régénération des plaques motrices après la section des nerfs. Travaux du laborat. de rech. biolog. publ. par S. R. CAJAL, Tome V, 1907.

[2]) ERIK AGDUR: Ueber Stückfärbung mit Bielschowskys Silberimprägnations-methode. — Einige Modifikationen. Zeitschr. f. wiss. Mikrosk. u. f. mikrosk. Techn., Bd. 34, 1917.

description. The accompanying figures give an idea of the appearance of the sympathetic nerves and their terminal organs on the ordinary cross-striated muscle fibres.

Figures 1, 2, 3, and 4 are drawn from preparations of the mm. interossei mentioned above. (I have drawn the figures with the help of the following optical aids — ABBE's drawing apparatus and LEITZ immers. $^1/_1$, a ocul. 4 for figs. 1, 2 and 3, REICHERT's drawing apparatus and ZEISS apochr. homog. immers. 2 mm. apert. 1.3 comp. ocul. 6 for fig. 4). On account of the operations that the animal had been subjected to, and on account of the length of the period of degeneration there is reason to assume that the intact nerves which are found in the preparations and which are reproduced in these figures are of a sympathetic and post-ganglionar nature — this is more especially the case, as I also obtained similar results in the animal that had undergone the corresponding operation, but in which the period of degeneration had been ten days.

The preparation on which fig. 1 is based shows at d) a degene-rated spinal nerve that ends in a similar degenerated motor plate on
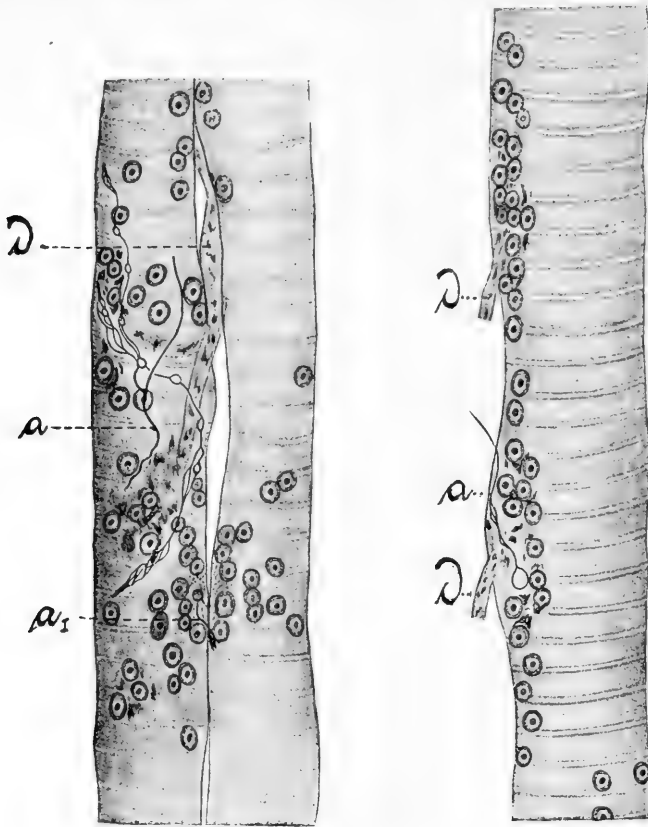
Fig. 1.   Fig. 2.

the left muscle fibre. At a_1 we have an intact sympathetic nerve
that ends with a loop in a degenerated motor plate. At a the prepa-
ration has an intact sympathetic nerve that passes away along the
left muscle fibre forming loops and varicosities. This nerve fibre
has no terminal loops in this preparation, but at one place half
way between a and d a part of the extension of the nerve fibre is
connected with a periterminal network and seems on this account
to be situated hypolemmally.

The preparation that forms the basis of fig. 2 shows, among other
things, a muscle fibre with two degenerated motor terminal plates.
These terminal plates are clearly situated on the same muscle fibre
and are at such a distance from each other as one generally sees
in plurisegmental spinal innervation of separate cross-striated muscle
fibres. An intact sympathetic nerve (a) with a simple loop formation
terminates within the region of the motor plate (d). There are thus
instances of sympathetic nerve fibres in the musculature of the
extremity as well, that terminate within the region of a motor plate.

Figure 3 is drawn from a preparation that shows one degenerated
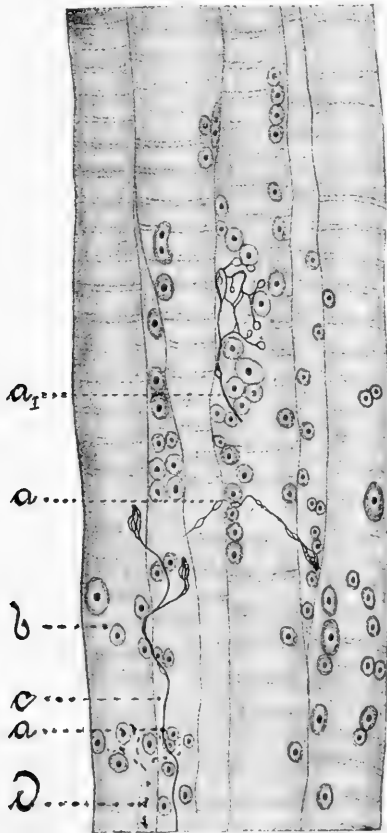
Fig. 3.　　　　　Fig. 4.

spinal nerve (d) low down to the left. The others are intact sympathetic nerves that pass away with the formation of loops and varicosities along the muscle fibres (a and aᵢ) or over and across these (a). I could not show any terminal loops or other connections with the interior of the muscle fibres in this preparation in the case of the nerve fibres a. The nerve fibres a_I, on the other hand, end in a terminal plate with rather abundant ramification. In this, as is shown by the figure, the different nerve fibres come to an end with almost circular terminal loops. At a couple of places in this plate there appeared a connection between the coarser neurofibril net and a peri-terminal network, which of course is in favour of a hypo-lemmal position for the sympathetic plate. This sympathetic terminal plate (a_I) is rather remarkable. Its great extension and its abundant neuro-fibrillar ramifications might easily lead one to suppose that we are concerned here with an ordinary motor terminal plate. That this is, however, not the case is shown, first, by the slender *non-medullated* nerve-fibre, a_I, which can be followed in several preparations (as the preparation belongs to a continuous series) and secondly by the fact that the nerve is intact after the operation mentioned above and after a long period of degeneration.

The preparation from which figure 4 is drawn shows, among other things, a muscle fibre with a degenerated motor terminal plate and a short distance (less than the length of the plate in question) from it another terminal plate of a nerve. This last terminal plate must consequently be of a sympathetic character to the preceding one. It is certain that the two terminal plates are situated on the same muscle fibre. We see here the interesting fact that two terminal plates of nerves, *a motor one* and a *sympathetic one*, the former degenerated and the latter intact, and the sympathetic terminal plate having also a great extension on the muscle fibre, are situated on the same muscle fibre and are at a distance from each other such as one finds between the motor terminal plates in a spinal pluri-segmental innervation of the separate muscle fibres [1]). In my opinion, however, it is as a rule easy to distinguish, even in preparations where all the nerves are intact, between motor and sympathetic terminal plates of nerves and thus to decide, when several terminal plates of nerves occur on the same muscle fibre,

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[1]) ERIK AGDUR: Morphologischer Beweis der doppelten (plurisegmentalen) motorischen Innervation der einzelnen quergestreiften Muskelfasern bei den Säugetieren. Anat. Anz. Bd. 49. 1916.

ERIK AGDUR: Ueber die plurisegmentellen Innervation der einzelnen quergestreiften Muskelfasern. Anat. Anz. Bd. 50, 1919.

whether there is a motor double innervation or a double innervation by means of a motor and a sympathetic terminal plate. This point will be discussed at greater length in a future and more detailed account.

Summary.

All the spinal nerves, whose ventral ramifications form the plexus brachialis, have in some cats been cut off between the spinal ganglion and the place where the ramus communicans albus goes off. When from five to ten days had elapsed after the operation, the animals were killed. In sections of Ag.-impregnated mm. interossei from the anterior extremity on the side operated on I found that all the nerve fibres that had medullary sheaths were degenerated, but that there were fairly numerous intact nerve fibres without medullary sheaths. On account of the operations the animals had undergone and the existing period of degeneration in the spinal nerves that had been cut off I have reason to believe that these intact non medullated nerves are of a sympathetic and post-ganglionar nature. We are thus faced by the exceedingly interesting fact that the cross-striated muscle fibres, even in the muscles of the extremity, are innervated by n. sympathicus — corresponding to what BOEKE showed morphologically to be the case for the inner orbital muscles (m. obliquus oculi superior). These sympathetic nerves in the extremity musculature terminate in comparatively simple loop – formations partly (among other places) on ordinary cross-striated muscle fibres and partly on muscle fibres in the muscle spindles. I have reason to believe that the great majority of these sympathetic terminal plates — both on ordinary muscle fibres as well as on those in the muscle spinalles — are situated hypo-lemmally — just as BOEKE described them in, among other places, m. obliquus oculi sup. of the cat. I have also, however, preparations which indicate that there are also epilemmally situated sympathetic terminal plates in the extremity-musculature. A number of the sympathetic terminal plates on ordinary cross-striated muscle fibres are situated within the region of extension of the motor plates, but the majority lie outside it. Among the sympathetic terminal plates that are situated outside the region of the motor plates I have examples of some that have a rather large extension on the muscle fibres and on account of this, approach the motor terminal plates.

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Anatomy. — *"Once more the innervation and the tonus of the striped muscles"*. By Dr. J. G. Dusser de Barenne. (Communicated by Prof. J. Boeke)[1]).

(Communicated in the meeting of January 29, 1919).

In continuation of a previous communication[2]), to which I think I may refer by way of introduction, I want briefly to revert to this question.

In the first place to communicate some further experimental facts and in the second place to recall my criticism on a communication by G. Mansfeld and A. Lucáks[3]), now that I have come to the conclusion that the former is not sound.

In that previous paper I have proved that S. de Boer's opinion, that the tonus of the striped muscles should be governed by the sympathetic nervous system, is incorrect. That further neither the cadaveric-rigidity, nor, as has already been shown by me[4]) before and has been confirmed by van Rijnberk[5]) since — the decerebrate rigidity have anything to do with sympathetic innervation. Only a slight, though clear hypotonus of the muscles of the hindleg was perceptible with warm-blooded animals and frogs, after unilateral resection of the abdominal sympathetic.

The result with my cats was that this symptom only disappeared in the course of 5 to 8 weeks. So I thought I had better not consider it a shock-phenomenon and as none of the other, in my opinion plausible explanations were decisive[6]), I had to leave

[1]) The experiments communicated here, were partly performed by Mr. H. J. Havik, med. stud. at Leiden, during my stay at Delft in the winter of 1917/1918.

[2]) Ueber die Innervation und den Tonus der quergestreiften Muskeln. Pflüger's Archiv, Band **166**, 1916, p. 145.

[3]) Untersuchungen über den chemischen Muskeltonus. I. Pflüger's Archiv, Band **161**, 1915, p. 467.

[4]) Ueber die Enthirnungsstarre (Decerebrate rigidity Sherrington's) in ihrer Beziehung zur efferenten Innervation der quergestreiften Muskulatur. Folia Neurobiologica, Band **7**, 1913, p. 651.

[5]) Recherches sur le tonus musculaire et son innervation, II. tonus musculaire et rigidité de décérébration. Archives néérlandaises de physiologie de l'homme et des animaux, tome I, 1917/1918, p. 726.

[6]) Cf. for l.c. (Pflüger's Archiv.), Bd. 166, p. 166 and 167.

this experimental fact unexplained for the present. For this reason I thought I was right in not rejecting absolutely the supposition that the sympathetic nerve would partially influence the tonus of the striped muscles. Since that time two communications by E. Th. von Brücke[1]) have been published from which it appears that he too has been able to observe initial hypotonus of the same kind in the acute experiment as was evident in my animals; but only during some days, after which the hypotonus disappeared altogether.

If this result should prove to be right in the greater number of the cases, the long duration of that initial hypotonus in my experiments would certainly have to be made dependent on other factors, which however would have nothing to do with the tonus as such.

With this the last support of de Boer's theory would drop.

For not only it has been proved that neither rigor mortis nor decerebrate rigidity are due to the sympathetic nervous system but besides this it has become evident to me that another phenomenon — mentioned by de Boer as being governed by the sympathetic — has nothing to do with it.

The "nose of Funke" occurring again and again in the muscle contraction curve was to disappear after extirpation of the sympathetic nerve chain.

After this resection I very often distinctly observed the "nose of Funke" in the muscle nerve of the frog, both with electrical and mechanical stimulation of the spinal cord, not only in the acute experiment, but also if the extirpation of the sympathetic chain, was done 2 months before the actual experiment and the post-ganglionic sympathetic nervefibres had degenerated.

This positive fact is of course decisive in face of the negative one of de Boer.

Three curves stating this experimental fact follow below.[2])

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[1]) J. Negrin y. Lopez and E. Th. von Brücke. Zur Frage nach der Bedeutung des Sympathicus für den Tonus der Skelettmuskulatur. Pflüger's Archiv, Band **166**. 1916, p. 55.

E. Th. von Brücke. Neuere Anschauungen über den Muskeltonus. Deutsche medizinische Wochenschrift, 1918, N°. 5 and 6.

[2]) In order to prevent a possible misunderstanding, I want to make the following remarks. The appearance of the "nose of Funke" in the muscle curve is often very variable. Sometimes it appears very distinctly as a second top in the curve. As is visible in fig. 1, very often its presence is only obvious from the fact that the duration of the muscle contraction curve is much longer than the duration of the single muscle contraction as in fig. 2 and 3. Between these all kinds of transition forms are to be found, also with respect to the place in the curve, where

When I published this communication[1] à propos of VAN RIJNBERK's tabular scheme[2] the latter[3] maintained that the fact of the "nose of FUNKE" still occurring after extirpation of the sympathetic does not prove in the least that the stimulations which cause this phenomenon, do not travel by the sympathetic fibres, when they are uninterrupted.

Little is to be said against this argument, but on examining it closely, it is yet somewhat sophistical. I am of the opinion that, when during an experiment a phenomenon occurs, notwithstanding the experimental circumstances and conditions, one has a right provisionally to draw the conclusion that the phenomenon concerned is not dependent on those experimental circumstances and conditions.

What value VAN RIJNBERK attaches to his own objection is evident from the fact, that, if he had thought it serious, he would have left his own essay on the connection between sympathetic innervation and decerebate rigidity unwritten. Furthermore does he himself sin against it in the same table, a few lines higher. For he ought at least to have put a? after the sympathetic genese of the second veratrine top. This one indeed is also present after extirpation of the sympathetic.

VAN RIJNBERK does not however infer from this, as one might expect from his above-mentioned reasoning that therefore stimulations causing the second veratrine top under normal innervation conditions might travel along the sympathetic fibre, but he concludes that the sympathetic has nothing to do with the second top.

This last reasoning and experimental fact are quite in harmony with my own opinion and experience. For it has been proved that both during the acute experiment and the chronic, when the sympathetic nerve fibres are degenerated, the second veratrine top still occurs in the muscle contraction, caused by stimulation of the spinal cord, either electrical or mechanical.

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the nose occurs Cf. for this viz. T. GRAHAM BROWN. Pflüger's Archiv. Band 125, 1908, p. 491. We do not know yet what is the meaning of the "nose of Funke". In my opinion it is not impossible that several different phenomena are hidden behind this. For the sake of brevity I used the term "nose of Funke" without pronouncing as my opinion that this is a well known single phenomenon.

[1] Spiertonus en ontherseningsstijfheid. Nederl. Tijdschrift voor Geneeskunde, 1917, I, p. 1756.

[2] VAN RIJNBERK. Spiertonus en ontherseningsstijfheid. Nederl. Tijdschr. voor Geneeskunde, 1917, I. p. 1634.

[3] Answer of VAN RIJNBERK to the remark cited Nederl. Tijdschrift voor Geneeskunde, 1917, I, p. 1757.
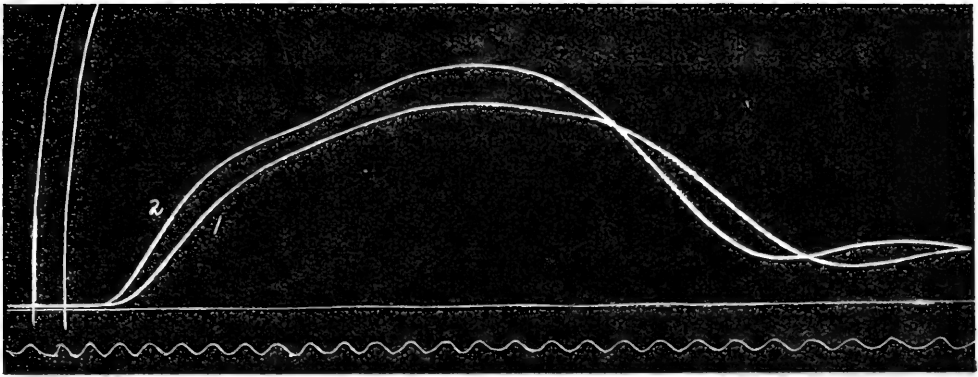
Fig. 1. Experiment B₁.

Frog. Acute experiment. *Right* sympathetic chain extirpated (under narcosis of ether) from N. V. to N. XI inclusive. Curves registered half an hour after the resection. Electrical stimulation of the cross section of the caudal part of the spinal cord with "make induction shock". In primary circuit $3^1/_2$ volts. In secondary circuit, except the resistance of the substance of the spinal cord, a resistance of 60.000 ohm, distance of coils 50.5 mm., small inductorium. Loading of the muscles about 12 grams. Curve 1 of *left* gastrocnemius. Curve 2 registered by *right* gastrocnemius.
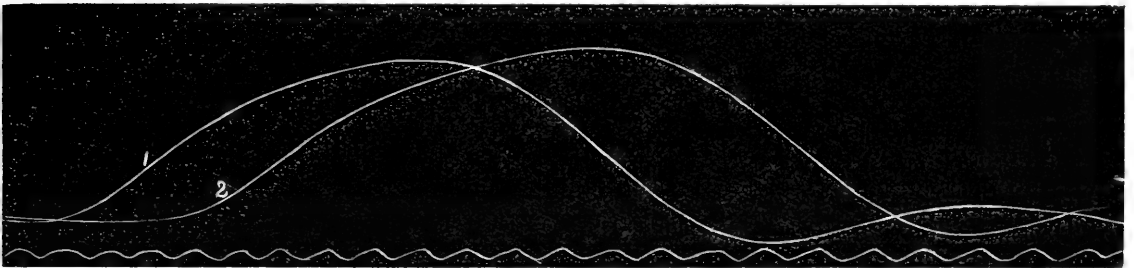
Fig. 2. Experiment C 28.

Frog. Acute experiment. *Right* sympathetic chain extirpated (under narcosis of ether) from N. IV to N. XI inclusive. Curves registered 45 minutes after resection. Temperature room $11^3/_4$ ° C. Mechanical stimulation of the spinal chord several segments above the origin of the roots of the Nn. ischiadici by the prick of a pin. Time curve $= ^1/_{50}''$. Loading of the muscles about 12 grams. Curve 1 of *right* leg, curve 2 of *left* leg.

Fig. 3. Experiment B 2.

Frog. Acute experiment. *Right* sympathetic chain extirpated under narcosis of ether from N. IV to N. XI inclusive. Curves registered 32 minutes after resection. Mechanical stimulation of the spinal cord far above the origin of the roots of the legnerves. Loading of the muscles about 12 g. Curve 1 of *left* gastrocnemius, curve 2 of *right* gastrocnemius.

Wherever it occurs with degenerated endplates, at the same time another plausible genese of that top, to which I alluded [1]) before but which I already thought improbable, appears to be inconsistent.

In the acute experiment one might always suppose that owing to the muscle contraction indicated by the first top, the undegenerated sympathetic endplates in the acute experiment are stimulated in the muscle itself and thus cause the second top by secondary peripheral stimulation.

When we take into consideration all the facts published until now on the tonus question in connection with the double innervation of the striped muscles — which van Rijnberk neglected — we come to quite a different view from the one van Rijnberk has given us in his table. I will first reproduce the table of van Rijnberk, then a similar one, which in my opinion offers the right data in this respect. Several of the extraordinary altogether enigmatical contradictions from van Rijnberk's table have disappeared in my table.

Table of van Rijnberk on p. 740, Archives néerlandaises l.c.

	Chimisme, augmentation de créatine.	Innervation.		Type du tonus.	
		Sympatique.	Musculo-motrice.	Plastique.	Contractile.
Rigidité de décérébration	+	cert. pas	+	cert. pas	+
Rigidité cadavérique	+	+		+	
Tonus de Brondgeest	+	+		+	+
Tonus de raidissement	+	?	+		+
2e sommet de vératrine.	+	cert. pas	+	cert. pas	+
Contract, chaleur.—Ca Cl$_2$ . . .	+			pas examiné.	
Tonus du froid	+				
Nez de Funke	pas examiné.	+		+	

Right table in my opinion.

	Chimisme, augmentation de créatine.	Innervation.	
		Sympatique.	Musculo-motrice.
Rigidité de décérébration	+	—	+
Rigidité cadavérique	+	—	+
Tonus de Brondgeest (tonus méchanique)	+	— (?)	+
Tonus de raidissement (tonus volontaire)	+	pas examiné.	+
Nez de Funke	pas examiné.	—	+

I left out the other facts, mentioned in the columns of the table of van Rijnberk,

[1]) D. de B. Ueber die Enthirnungsstarre u.s.w. Folia Neurbiologica, Band 7, 1913, p. 653 and 654

which I reproduced here. The forms of muscle-shortening indicated in these, perhaps or even probably arise from stimulation of the muscle-substance itself, so they have a muscular origin, in which the nervous system does not play any part. I left out the columns on the two types of tonus after LANGELAAN, because his division does not agree in my opinion, with several physiological facts. (See the criticism in my communication on muscletonus in PFLUGER's Aichiv, Bd. 166, p. 163—165). I put the? in the second column of my table referring to the initial hypotonus in the acute experiment (DUSSER DE BARENNE—VON BRÜCKE).

Although it has appeared that none of the views uttered by DE BOER in this question is right, I have still tried in some other experiments to obtain proofs in favour of the supposed connection between muscle tonus and sympathetic innervation. My reasoning was the following: Supposing that the sympathetic nervous system has something to do with the mechanical muscle tonus, with the inward support of the muscles, then we might expect that some proof of this will appear in the musclecurves of fatigue or in curves illustrating the origin of tetanus by stimulation of increasing frequency. The result of these experiments was however quite a negative one, i.e. neither in the acute experiment, nor in the chronic one with degenerated sympathetic endplates, was there any essential difference in the muscle curves of the 2 gastrocnemii, of which one was deprived of its sympathetic innervation.

In the acute experiments the two largest ventral roots of the Nn. ischiadici were put on the electrodes, to stimulate the nerves centrally of the sympathetic chain aiming to avoid the post ganglionic neurones from being stimulated. In the chronic experiments the Nn. ischiadici were stimulated in the abdomen.

Small differences between the 2 curves of fatigue were perceptible, but these did not point in all cases in the same direction. In some cases the "Verkürzungsrückstand" in the muscles deprived of their sympathetic innervation was less evident than in the normal gastrocnemius. In other cases just the opposite took place. Besides, curves, taken as a test, of the 2 gastrocnemii of normal frogs, often showed similar small differences. It is noteworthy that all precautions were taken in these experiments to obtain a great regularity and equal intensity of the stimulations. I used therefore an induction apparatus with the usual waterwashed mercury contacts after KRONECKER. A very considerable resistance was interpolated in the secondary circuit (120.000—150.000 Ohm). The stimulations were given by a metronome. Thanks to all these precautions the curves generally showed a beautiful regularity. The stimulations were always either make — or break — induction shocks; the impulses of contrary direction were eliminated by the well-known method of PFLÜGER.

Also in similar experiments on the genese of tetanus, no essential differences pointing in one special direction between normal frog muscles and those deprived of their sympathetic innervation, could be observed.

We come therefore to the conclusion that until now not a single experimental fact exists, pointing clearly to a direct connection between the mechanical tonus of the muscles in the sense of BRONDGEEST, and the sympathetic nervous system. As regards to the initial hypotonus occurring in my experiments, the solution of this question ought to be given by further experiments. Special attention ought to be drawn to the fact already mentioned, that this hypotonus in the experiments of v. BRÜCKE disappears already some days after the extirpation of the sympathetic. At all events the communication of VON BRÜCKE has considerably weakened DE BOER's theory. This as regards the mechanical muscle tonus.

I have now to refer briefly to the chemical muscle tonus. G. MANSFELD and A. LUKÁCS [1]) communicated experimental facts from which they derive the existence of a so-called chemical muscletonus, by which term is expressed the view that striped muscles would have a certain amount of metabolism, also when they are at rest. This metabolism would be under the influence of the sympathetic nervous system. At first I thought [2]) that the experiments, published by these investigators, were not convincing, and lately I briefly explained [3]) my former objections against them.

Since I have come to the conclusion that the criticism given by me is not sound, I recall it. All the same, the authors might have based their result even better, if they had made direct gasanalyses of the blood streaming to and from the muscles concerned. If the result of these analyses should confirm their former results, only then there could be no more doubt with regard to the accurateness of their result [4]).

The objection might yet always be raised against the respiratory analyses executed on the whole animal, that their result might be dependent on the fact, that by the extreme vaso-dilatation in the hind part of the body of their animals, too little blood remained in the fore part of the body, to preserve a fit exchange of gas in the muscles there, so that the respiratory metabolism might

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[1]) l.c.

[2]) Pflüger's Archiv. Bd. **166**, 1916, p. 152.

[3]) Archives Néerlandais de Physiologie, tome II, 1918, p. 177.

[4]) A similar method as the one used by LANGLEY and ITAGAKI for their experiments on the oxygen use of denervated muscle, came into consideration (Journal of Physiology, **51**, 1917, p. 202).

considerably be lessened by too small an exchange of blood within these muscles. This factor eventually might have lowered the total gasexchange of their animals, as has been shown by their experiments.

Whether this objection has any ground cannot be made out without experiment, but it proves anyhow, that the experiments by MANSFELD and LUKÁCS are as yet not indisputable.

Until now we always accepted as a fact in all the experiments and speculations communicated, that the sympathetic nervefibres of BOEKE are centrifugal sympathetic nervefibres, a supposition for which several very evident histological arguments might be cited, but which has not been proved, as I said already once more.

This has been proved lately by a research ad hoc by Prof. BOEKE and me and besides by some similar experiments, made independently of us by AGDUHR.

If those nervefibres of BOEKE were indeed centrifugal sympathetic nervefibres, then it ought to be possible to preserve these in "pure culture" in the striped muscles, by section of the ventral nerve roots leading to one or more muscles, and extirpation of the corresponding spinal ganglia. After this section all the cerebro-spinal motor nervefibres with their so-called endplates of KÜHNE together with all the sensory fibres and organs in the muscles concerned ought to degenerate.

Granting that BOEKE's fibres are centrifugal sympathetic nervefibres, whose praeganglionic neurones have their origin in the spinal cord, leave the cord with the ventral root and terminate round the cells of the post-ganglionic neurones in the ganglia of the sympathetic chain those fibres of BOEKE ought to remain unaltered in a similar experiment. A look on the following scheme illustrates the conception on which these experiments are based. (Fig. 4).

The intercostal muscles of dog and cat have served as object for this experimental histological investigation, because the metameric arrangement has been best preserved in these muscles. There is no fear here for confusion caused by the plurisegmental innervation. The result of these experiments has been, that the nervefibres and endplates of BOEKE remained intact in the muscles between the ribs. All the motor cerebro-spinal nervefibres and endplates, as well as the sensory muscle-organs had disappeared.

Numberless amyelinic axiscylinders were preserved in the peripheral nerves (intercostal nerves) and beautiful accessory nervefibres and endplates of BOEKE in the muscles. By this result it has been proved that these nervefibres are indeed *centrifugal* sympathetic nervous systems.

AGDUHR obtained the same result with the muscles of the hindleg of the cat by section of the peripheral nerves distal of the spinal
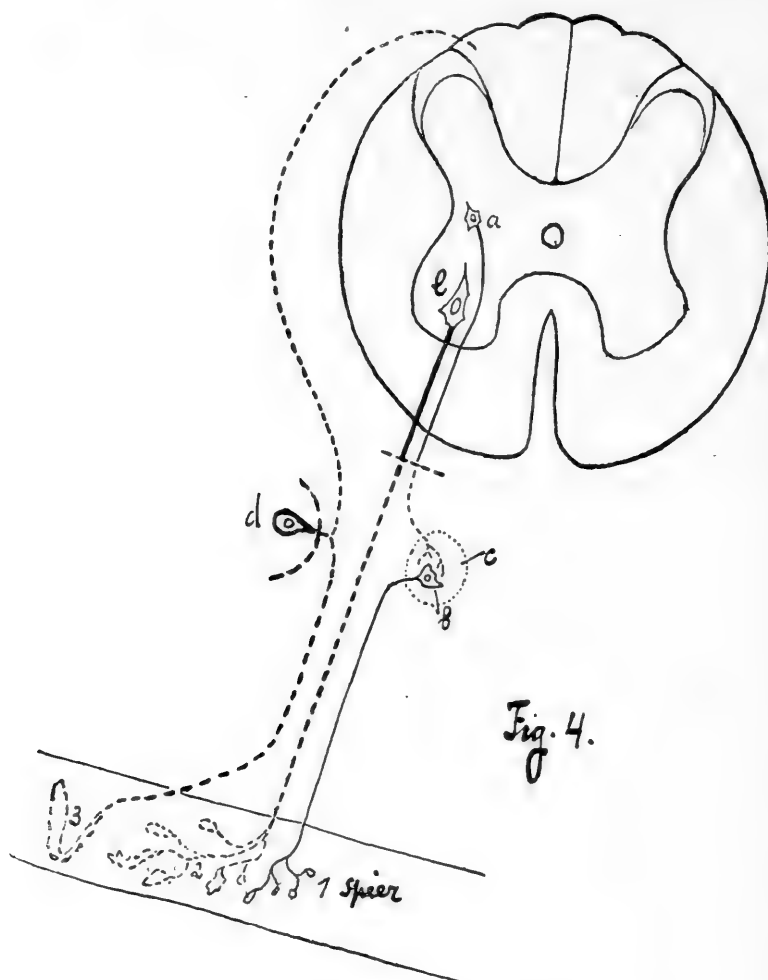
Fig. 4.

a := nervecell of the praeganglionic sympathetic neurone.
b = nervecell of the postganglionic sympathetic neurone.
c = ganglion of the sympathetic chain.
d = the spinal ganglion cell.
the degenerated nervefibres have been drawn in a blocked line.
1 = accessory endplate of BOEKE, preserved in "pure culture".
2 = degenerated endplate of KÜHNE (the ordinary motor endplate) (disappeared).
3 = degenerated sensory organ in the muscle (disappeared).

ganglia, but central of the origin of the rami communicantes grisei. [1]
The question that arises is consequently: What is the function of the fibres and accessory endplates of BOEKE?

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[1] See the foregoing communications.

After all we know about it, it is very improbable that they have anything to do with the mechanical muscletonus, known as the BRONDGEEST tonus. It is very probable that this one is exclusively due to the simple motor nervefibres. While considering this, the "chemical muscletonus" occurs to us, the existence of which and its dependence on the sympathetic nervous system, if not proved, is certainly not made unplausible by MANSFELD and LUKàcs. When we realize these two hypotheses, most of the difficulties and strange contradictions, created by DE BOER's theory, which are evident in VAN RIJNBERK's table, disappear.

By the formula, just mentioned, the mechanical muscle tonus being governed by the cerebro-spinal nervefibres, the chemical one by the centrifugal sympathetic system of BOEKE, these difficulties disappear altogether and with them an important factor of confusion has been done away with. VAN RIJNBERK reproached me for having contributed only critical work with negative results; nobody better than I myself realize this; yet I believe that this work was necessary and I find the best argument for this in the two preceding hypotheses. I hope that these hypotheses will shortly be based on indisputable experimental facts. In my opinion everything points to it that this will be highly probable. I shall be the last to maintain that by these facts our knowledge of the nature of the tonus of the striped muscles has been much deepened. What the tonus really is, is as obscure and mysterious as before.

Physics. — *"The Unidirectional Resistance of Crystal Detectors"*. By M. J. Huizinga. (Communicated by Prof. H. Haga).

In a former communication (c.f. these Proceedings September-meeting 1916) the electrolytic phenomena of the molybdenite-detector have been described. These phenomena made it likely that the rectifying power in this crystal contact is not due to thermo-electric effects as is usually thought to be the case, but to the E. M. F. of electrolytic polarisation.

The question whether one is entitled to extend this conclusion also to other crystal detectors was discussed in my doctor-thesis (Groningen 5 Juli 1918).

The present communication gives the results there described.

§ 1. *Nature of the electrolytic products in the molybdenite-contact.*

If a platinum point is placed on a molybdenite-crystal and a current of about one milliampère is sent from the crystal to the platinum, a small quantity of a dark blue liquid will be developed. The spot of liquid will not expand with a stronger current, as the additional heat of the current brings about a quicker evaporation. Therefore repeatedly a tiny drop of distilled water was put on the place of contact and every time was sucked up again as soon as, usually after some seconds, it had got a dark blue colour. In this way a few c.c. of this solution were obtained. In the chemical Laboratory of Groningen (director Prof. Jaeger) this liquid was examined, leaving after evaporation a blue residue MoO_2, MoO_3, $6H_2O$; a colloidal substance which when exposed to the air, oxidised slowly into MoO_3.

If the current is sent through the detector in the opposite direction, e.g. from the platinum to the molybdenite, the brown substance developed can easily be obtained in large quantities by electrolysis of some diluted acid between electrodes of molybdenite. This brown colour must be attributed to the colloidal sulphides MoS_2, MoS_3.

§ 2. *Other detectors.*

A second detector-combination in which phenomena of electrolysis
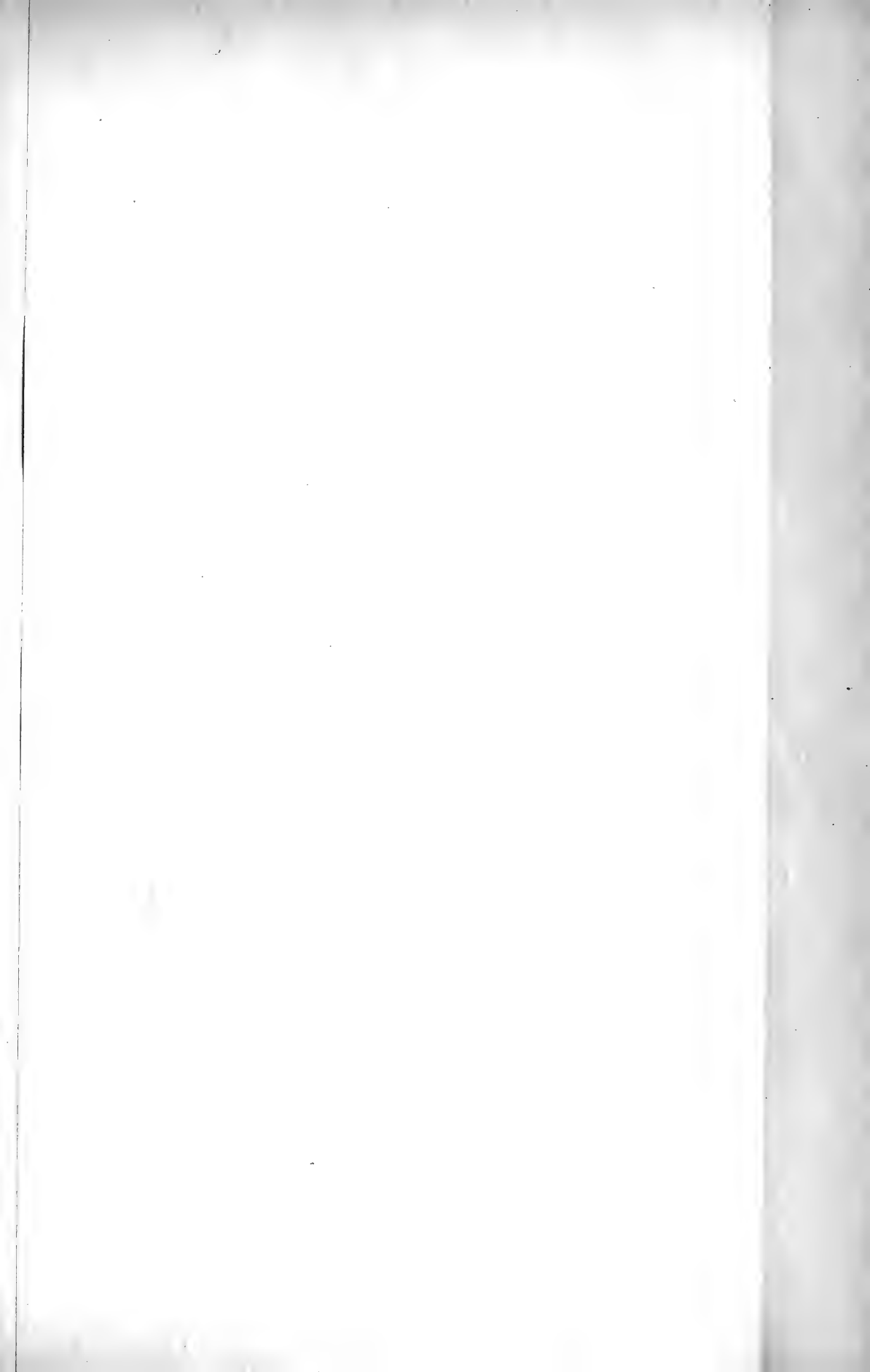
could be observed is that of ironpyrites and platinum; these pheno-
mena are most distinct when the place of contact is such as to
bring about the strongest unidirectional resistance. In this case the
current must flow from the crystal to the platinum needle, which
in this contact is the weaker current, in contradistinction to the
molybdenite-contact, a fact which is at once obvious from the perusal
of the characteristics of rectification (cf. below). Here the products
of electrolysis consist in a black and a colourless liquid, from the
latter of which colourless crystals usually secrete. The phenomena
of electrolysis are much weaker than in the molybdenitedetector.
The applied E. M. F. may not amount to more than 5 volts because
the unidirectional resistance together with the electrolysis will then
disappear. This disappearance of the unidirectional resistance has
already been found by FLOWERS for a galenacontact.

Galena, zincite, copperpyrites, copperglance, bornite and carbo-
rundum detectors were also examined. With these contacts no indi-
cation of any electrolysis was found. With galena only sometimes
a dark spot on the place of contact was visible. Though electrolysis
was brought about here by moisture, yet it usually stopped after
some moments on account of evaporation of the liquid. However,
every time the unidirectional resistance was considerably increased
through this operation, and the direction of greatest resistance
remained the same as in a fresh contact.

§ 3. *Experiments in vacuo.*

We were not far wrong in supposing that the unidirectional
resistance was the consequence of the electrolysis in a damp film
in which the originally imperceptible products of electrolysis, if
hygroscopic, can extract particles of moisture from the air, so that
the electrolytic products become visible. The latter would be the
case with ironpyrites and molybdenite.

A research in vacuo and in hydrogen showed that the unidirectional
resistance of the molybdenite detector continued to exist, the electro-
lysis, however, not being perceptible now. Nevertheless the uni-
directional resistance may in this case still be attributed to an adhering
layer, for this layer can only be removed with difficulty and
evidently evacuation is [wholly] insufficient to effect this.

The unidirectional resistance continued to exist also under a layer
of paraffin oil, while it was also impossible here to discover the
electrolysis. However, from this experiment the inference should
not be drawn that the electrolysis is only a secondary phenomenon
not causally connected with the unidirectional resistance.

This does not become obvious unless one draws the characteristics of rectification representing the relation between the E.M.F. applied to the contact and the current passing through.

§ 4. *The observations for the characteristics.*

As the intensity of the current passing through is not only a function of the applied E.M.F. but also depends upon the time the current has already passed, the characteristic curve will be found to alter with time. One must therefore determine the curve by means of a sufficient number of observations, all of them taken within as short a time as possible. As mirror-galvanometers are generally too "slow", "Präzisionsinstrumente" of Siemens and Halske were used,
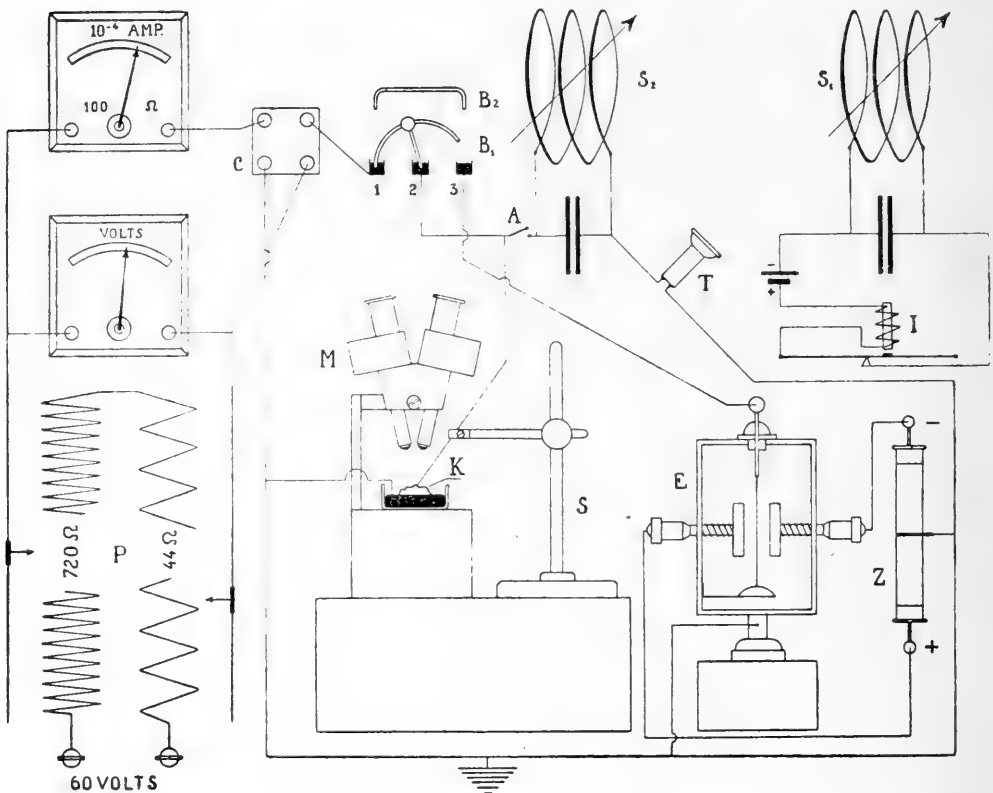
Fig. 1.

which indicate the exact intensity of the current instantaneously and, as they are pointing instruments, are easy to read.

The connections are shown in Fig. 1. The crystal K usually floated on mercury which formed at the same time the one electrode.

By means of the binocular microscope M the place of contact could be examined. This figure also shows that by means of the copper-wire B_1 the detector could be brought into contact with the Wulf-electrometer E. In order to know to what voltage the displacement of string corresponded, the electrometer was connected to the poten-tiometer P, by replacing B_1 by the u-shaped B_2, thus connecting the mercury cups 1 and 3. After the electrometer had again obtained the same deflection, the voltage was read from the voltameter. More-over the contact could be tested as a detector. To this end electric oscillations were excited in the system S_1 and induced into the system S_2. By removing B and making the contact A, the detector was brought into the system S_2 having a telephone T. Its action as a detector was judged by the intensity of sound in the telephone.

§ 5.   Characteristics of electrolytic detectors.

The characteristic of the electrolytic detector distinctly shows that the deviation from Ohm's law in this detector will have to be ex-plained by the counter E.M.F. of polarisation in consequence of electrolysis[1]). The characteristic (curve a in fig. 2) can be represented by the formula $I = \dfrac{E-e}{R}$, in which I is the current, E the applied E.M.F., and R a constant resistance, e the E. M. F. caused by pola-risation.

This E.M.F. of polarisation increases together with the applied E.F.M. and will reach a maximum of about 3 Volts, as indicated by curve b. As soon as the E.M.F. of polarisation has reached this maximum, the characteristic will change into a straight line inter-secting the horizontal axis at the point accurately representing the maximum value of the E.M.F. of polarisation.

This maximum found with the aid of the characteristic, may also be obtained by direct measurement with the Wulf electrometer. If this E.M.F. of polarisation did not occur, the characteristic would be represented by the straight line c through the origin, parallel to the straight part of curve a. If the applied E.M.F. is represented by the line OP, RQ will represent the E.M.F. of polarisation which can be deduced from the characteristic. The R may then be called the "real resistance" of the detector and $\dfrac{E}{I} = \dfrac{E}{E-e} R$ the "apparent resi-

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[1]) Armagnat. Journal de Physique, V, pag. 748, 1916.

stance". The real resistance is therefore represented by the angle which the straight part of the characteristic forms with the axis of
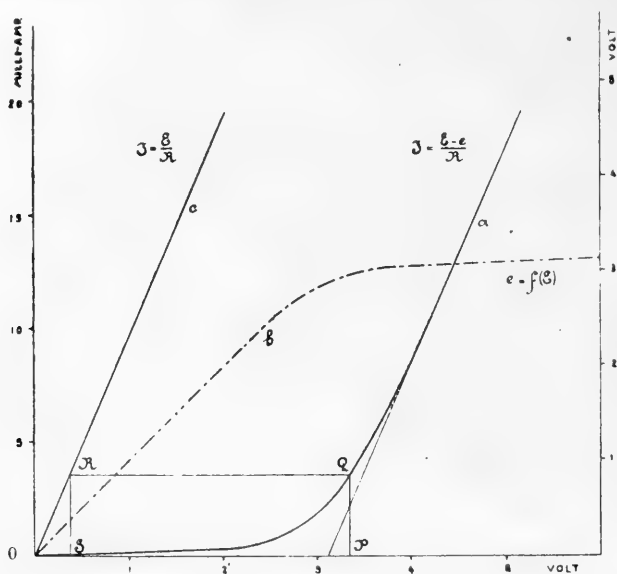
Fig. 2.

ordinates while the point of intersection of the extension of this straight part with the axis of abscissae indicates the maximum E.M.F. of polarisation. If the current is sent through this electrolytic detector in the other direction, the same curve will be obtained [1]), which for this detector is symmetrical with respect to the origin. When using a constant auxiliary E.M.F., the centre can be brought outside the origin. The same voltage will then yield a different intensity of current according to the direction in which it is applied, i.e. the electrolytic detector *with auxiliary E.M.F.* has a unidirectional resistance.

If the platinumpoint is replaced by a thin wire of copper or molybdenum the detector will also exhibit an unsymmetrical characteristic without any auxiliary E.M.F. It will then have the shape of the curve FI (cf. fig. 3 on the folding plate). The real resistance [2]) is equal in both directions as will appear from the fact that the two linear parts are parallel, but the maximum value of the E.M.F. of polarisation is different in the two cases and amounts to about

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[1]) The platinum point should not be taken too small here.

[2]) *Remark*. As the readings of the voltameter and milliammeter are plotted directly, the "real resistances" R derived from the characteristics of fig. 3 are all of them 100 Ohms too large, as obviously the resistance of the milliammeter (100 Ω) is included. This does not however influence the above discussion.

2,2 Volts, if the current passes from the sulphuric acid to the molybdenumpoint. It is about 0,75 Volt in the opposite direction. This much smaller E.M.F. of polarisation will according to ARMAGNAT be found if the anode consists of a metal soluble in the liquid.

A peculiar phenomenon, not observed by ARMAGNAT occurs when the molybdenum- or copperelectrode is reduced to half a m.m. or less. While the characteristic F II in the first quadrant changed but little — only the slope of the straight part will become smaller, hence the real resistance is increased —, the negative branch of the characteristic in the 3rd quadrant is straight and runs through the horizontal axis. Only when the applied $E. M. F.$ exceeds the amount of about 20 Volts a strong current may suddenly be observed. The high apparent resistance may then be restored again as soon as the applied $E. M. F.$ is decreased to the former value. The particular phenomena of electrolysis occurring in a very small electrode in consequence of strong current density evidently cause the dissymmetry so well to be marked here. The accompanying colloidal oxide $Mo_5 O_{14}$ points to a possible relation between these phenomena and those taking place in the aluminium rectifier. Indeed, the characteristic A of a rectifier, obtained by placing in a solution of ammoniasulphate an aluminium wire of 1 m.m. thickness and 1 c.m. length opposite a large platinum electrode, agrees with the characteristic F II. The rectifying power is attributed by SCHULZE and TAYLOR [1]) to a thin film of oxygen fixed by a layer of aluminium-hydroxide. SCHULZE also found the same behaviour for many other metals. In the 3rd quadrant the characteristic A remained horizontal to about 25 Volts. Usually the resistance suddenly diminished with a stronger $E. M. F.$, a layer of aluminium hydroxide detaching from the point. The rectifying power was restored again as soon as the applied $E. M. F.$ was diminished. CLARENCE GREENE [2]) has shown that the horizontal part of the characteristic of the aluminium rectifier is due to an $E. M. F.$ of polarisation counteracting the applied $E. M. F.$

Summarizing one may say that the characteristics of the electrolytic detectors generally have the shape of the curve F I with two parallel straight parts. It may happen that one branch is not fully developed. It is not necessary that the centre of the characteristic occurs at the origin.

§ 6. *Characteristics of crystal rectifiers.*

Molybdenite-platinum. In considering the characteristic of a

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[1]) A. H. TAYLOR. Wiedemanns Annalen 30, pp. 984, 998, 1016.
[2]) CLARENCE GREENE. Phys. Review, 2nd Ser. Vol. III, 1914.

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sensitive molybdenite-platinum detector E_1I, the straight part in the first quadrant is very prominent. This part was obtained by sending the current from the crystal to the point and was measured before the electrolysis had become perceptible. Evidently the curve may be represented again by the formula $I = \dfrac{E-e}{R}$, in which R is the constant real resistance and e a hypothetical counter E. M. F. That the real resistance is represented by the slope of the straight part appears when a series of very brief current impulses is sent through the contact. We then find successively the characteristics E_1 II and E_1 III, which in the first as well as in the third quadrant approach more and more to a straight line through the origin parallel to the straight part of the other characteristics. This will still be clearer when we consider the characteristics of a number of other detectors.

In this case also we may assume the existence of a counter E. M. F. with a maximum of about 1.1 Volts, though the latter could not be detected with the WULF electrometer. For, if the current is passed for some time longer, so that the electrolysis becomes clearly visible with the microscope, the characteristic of the contact changes from E_1 III to E_2 IV. If further the contact pressure is diminished, curve E_2 V will be obtained showing again clearly the unidirectional resistance. If finally this crystal, after some further electrolysis, is connected with the WULF electrometer a polarisator E.M.F. of 1.1 Volts will be measured. During this gradual transition of the characteristic E_1 I into E_2 IV *the real resistance remains constant* and this proves that the unidirectional resistance of the contact even without any electrolysis being visible, must be attributed to an electrolytic counter E. M. F. in an extremely thin film.

With strong currents the straight part becomes curved, the concave side being towards the vertical axis. In the 3rd quadrant no straight part can be obtained at all. This is due to the decrease of the real resistance of similar substances[1]) with rise of temperature. With molybdenite the conductivity is doubled already with rise of temperature from 0—200° C.[2]). It appears from the quick evaporation of a drop of oil placed on the point of contact that this rise in temperature caused by a current of 0.03 Amp. is considerable.

Carborundum-steel. With the very sensitive carborundum-steel detector no phenomena of electrolysis could be seen. Nor was it possible, except by applying a strong E. M. F. to change the charac-

[1]) O. REICHENHEIM, Ueber die Elektrizitätsleitung einiger natürlich kristallisierten Oxyde und Sulfide und des Graphits. In angural Dissertation, Freiburg 1906.

[2]) A. E. FLOWERS, Phys Review 1st. Ser., Vol. XVIII, 1909.

teristic D. The particular shape of the curve, especially in the first quadrant can hardly be explained in an other way than by a counter E. M. F. with a maximum of about 12.5 Volt.

Zincite-bornite. The characteristic G of a zincite-bornite contact corresponds exactly to curve F I. Exactly the same characteristics belong to the combinations zincite-copperpyrites and zincite-copperglance. The straight parts cut the axis at $-0,4$ and $+5$ Volts. If further a succession of current impulses is sent through, the straight parts of the characteristics undergo parallel displacements. The same shifting is found in the characteristics obtained by bringing every one of the components into contact with a platinum point.

Zincite-platinum. If a succession of current impulses was passed through, the curve C I gradually changed into the straight line IV. The slope of the straight part of curve I consequently gives the real resistance and further proves, in the way shown above, the existence of a counter E.M.F. of 0,4 Volt. Hence it follows that in the other direction a counter E.M.F. must be found as well. Indeed, with some characteristics a straight part did occur in the first quadrant, cutting the axis at about $+3$ Volts. The following characteristic e.q. was obtained.

From zincite to platinum

0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0	2.25	2.5 Volt
1	3	4	5	6.5	7	8	8.5	9	9.5×0.0001 Ampere

2.75	3.0	3.25	3.5	3.75	4.0	4.25	4.5	4.75 Volt
10	11	14	20	31	42	52	63	74×0.0001 Ampere.

From platinum to zincite

0.25	0.5	0.75	1.0	1.25	1.5	1.75	2.0 Volt
1.5	9	16.5	24	33	45	56	67×0.0001 Ampere

2.25	2.5	2.75	3.0	3.25	3.5	3.75	4.0 Volt
77	86	98	108	118	129	140	150×0.0001 Ampere.

Bornite-platinum. This combination shows the greatest resistance when the current passes from metal to crystal, see B I. A very slight impulse already causes the straight line B II to appear. The same curve is obtained by the combination copperglance-platinum and chalcopyrites-platinum. The straight part points to a counter E.M.F. of 0,4 Volt. It is remarkable that after reversal of the applied E.M.F., the current usually remains steady for about three seconds and then falls in a discontinuous way. The same phenomenon also occurs in other crystal contacts, but was most frequently observed with the electrolytic detector.

If we compare curve B I and C I, it is clear why the zincite-

bornite detector has such a strong unidirectional resistance. For, curve G may be regarded as a superposition of curves C I and B I, the latter first being turned 180°.

Zincite-molybdenite. In order to test this statement, the crystals zincite and molybdenite, each of which in combination with platinum exhibits such different characteristics, can be brought in contact with each other. That this contact has a very pronounced unidirectional resistance, appears from the following characteristic.

From zincite to molybdenite

1	2	3	4	5	6	7	8	9	10	11	12 Volt.
1	2	4	6	7	9	12	14	18	29	49	79 $\times$ 0,0001 Ampere.

From molybdenite to zincite

0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6 Volt.
1	5.5	15	26	39	51	64	75	86	98	110	123 $\times$ 0.0001 Amp.

Moreover it follows that the unidirectional resistance of the zincite-platinum contact must be attributed to the same cause as that of the molybdenite contact, e.g. to electrolytic polarisation.

Galena-platinum. A gelena detector usually yielded a characteristic agreeing with curve B I. Occasionally the characteristic agreed more with curve C I, the resistance being now greatest in the opposite direction. Both curves soon altered with time. Curve K I was obtained after a current of 0,005 Amp. had first passed during 15 minutes through the contact from the galena to the platinum, the contact pressure being very slight. It was not possible to extend the curve into the first quadrant because with too high a voltage the curve would again pass into curve III. If a current of 0.01 Amp. was now sent from platinum to galena during 15 minutes, the characteristic K II was obtained. Curves I and II clearly show that the real resistance of the contact is represented by curve III and is the *same* in all three cases. Curve I points to an E. M. F. of polarisation with a maximum of 0,25 Volt, whereas the maximum in the other direction could not be measured. Curve II points to two maxima; 1,4 Volt and 0,1 Volt. The existence of these two characteristics can hardly be attributed to anything else than to changes caused by the passage of the current through the contact which can only be of an electrolytic nature.

Ironpyrites-platinum. The characteristic H of an ironpyrites-platinum contact does not show anything new after the preceding. Electrolysis was only observed in this crystal under the microscope after we were satisfied, on the authority of the above considerations, that the unidirectional resistance is due to electrolytic polarisation.

Summary.

Electrolytic phenomena have been observed with the molybdenite detector and the ironpyrites detector; the $E. M. F.$ of polarisation is the cause of the difference of current intensity by reversal of applied $E. M. F.$

The characteristic curves for these detectors were compared with those of other crystal detectors and of the electrolytic detector. From the similar shapes of the characteristics it has been concluded that with all the crystal detectors examined, though no products of electrolysis are visible, the unidirectional resistance is to be attributed to electrolytic polarisation in a moistened- or a gasfilm adhering to the surface.

The resistance of most of the crystal detectors employed in wireless telegrapy is less than it is usually thought, and as a rule does not exceed 100 Ohms.

E R R A T A.

Proceedings Vol. XXI n°. 8.

Page 1066, line 1 from bottom: For "and" read "for".

Page 1067, line 2: For "this ceases after some time. When the voltage is raised further", read "this ceases after some time. The wall of the bulb however has got covered by a gray-blue layer. When the voltage is raised further,"

Page 1067, line 3: For "glass" read "deposit".

Page 1067, line 4: For "layer is vaporized" read "is formed". For "By this vaporized material the bulb wall becomes" read "By this vaporising of material however the bulb wall becomes".

Page 1067, line 5: For "Now this" read "so that the"

Page 1069, line 14 from bottom: For "hydrogen" read "water-vapour".

Page 1069, line 12 from bottom: For "volume f" read "volumeter f".

Page 1071, line 12 from bottom: For "the oxides do not remain therefore oxides" read "the oxide dissolves in the glass".

Page 1072, line 19: For "G. conclusions" read "G. concluding remarks".

Page 1073, lines 2 and 3 from bottom: For "**25**, 661 (1916), **26**, 595 (1917)" read "**19**, 958 (1916), **20**, 1136 (1917)".

Page 1074, lines 13 and 14: For "that part of the troublesome gases in a glow-lamp are only liberated" read "that only a part of the troublesome gases in a glowlamp is liberated".

Page 1074, line 19 from bottom: For "$Cu_3 (PO_4)_2$" read "$Ca_2 (PO_4)^2$".

Page 1074, line 18 from bottom: For "magnesium-sulfate" read "magnesium-aluminate".

Page 1074, lines 3 and 2 from bottom: For "Thus the CaO — when such a silicate is used — from the glass will be sublimated" read "Thus the CaO from the glass — when such a silicate is used — will be sublimated".

Page 1075, line 23: For "gradual" read "after some time".

CONTENTS.

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Physics. — *"On thermoelectric currents in mercury"*. By Prof. H. Haga and Dr. F. Zernike.

In an extensive paper "Ein für Thermo-electrizität und metallische Wärmeleitung fundamentaler Effect", [1] C. Benedicks endeavours to show the existence of a thermoelectric force in a homogeneous conductor, when at both sides of a heated part the temperature falls off at a different rate, i.e. the temperature gradient is different. [2] He makes due allowance for the possibility of the thermo-electric force which appears under these circumstances in solid conductors being due to changes of structure, which would make the contiguous parts of the conductor behave as different substances. Therefore he considers the proof of the reality of the force mentioned to depend upon the success of experiments with a liquid conductor. To this end he used a glass tube filled with mercury, which had been drawn down at one point, and heated the wider part next to it, thus bringing about a high temperature with slow decrease in the wide part, and steep gradient at the constriction. He did not obtain reliable results from these experiments, which he supposed to be caused by the conduction of heat through the glass. This would heat the mercury in the narrow part and thus prevent the temperature from falling off with sufficient steepness. Against the well-known experiments of Magnus, who could not detect any current in bringing into contact mercury conductors of different temperature, and who worked also with unequal temperature gradients, Benedicks advances the low sensitiveness of Magnus's pointer-galvanometer compared with the mirror galvanometers of the present time.

We have devised an experimental method by which, while using mercury, all the conditions of Benedicks for a sensitive test [3] would be met, thus enabling us to get a conclusive decision as to the reality of the new effect. This method consists in the use of two mercury jets joined to a sensitive galvanometer, one of them

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[1] Ann. der Physik. **55**, p. 1—80, p. 103—150. 1918.

[2] Pogg. Ann. **23**, p. 497, 1851. Magnus here tried to disprove the production of thermo-electric currents under these circumstances.

[3] l. c. p. 118.

being heated. The influence of the wall, feared by BENEDICKS, is thus completely eliminated; the surface of contact can be made very small and in this surface the mercury is continuously renewed, thus making the temperature gradient very large and stationary.
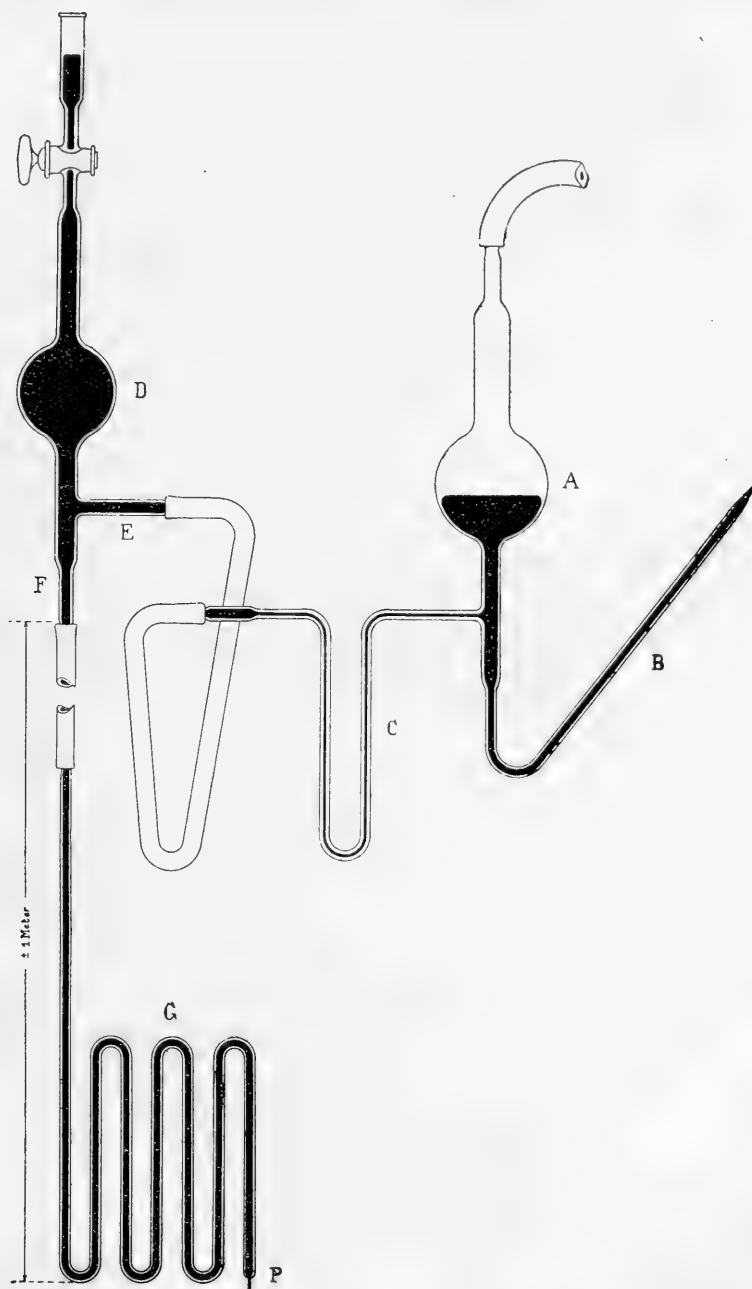
The accompanying figure shows the arrangement used. To a glass bulb *A* is attached a tube *B*, the end of which has been

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reduced to a small aperture in the blow-flame. C is a capillary joined to half a metre of rubber tubing, which leads to E. D, E, F form together a second glass part; the lower end of F is joined through another half metre of rubber tubing to G, which is bent three times up and down. At P a platinum wire has been sealed into the glass tube.

Half of bulb A and all the rest of the glass apparatus was filled with mercury distilled in a vacuum. A stout rubber pressure tube was slid over the narrowed top of A and joined at the other end to a reservoir in which air had been brought to a pressure of 2 to 3 atmospheres. The arrangement described served the double purpose of preventing heat being carried by conduction from the heated tube B to the platinum wire P, and also procuring an easy way for refilling bulb A with mercury.

For each mercury jet a similar apparatus had been prepared. The two parts G were tied together and placed in a vessel with water. ($48 \times 24 \times 20$ cm.). To the platinum wires P were soldered the ends of flexible wires covered with rubber and silk, leading to the galvanometer, the junctions and the bare platinum and copper ends being thickly coated with shellac. Two metres of the leads were immersed in the water, thus preventing any conduction of heat either through the mercury or through the copper, and securing perfect equality of temperature of the two mercury-platinum-copper junctions. The resistance of the connecting wires, the tubes with mercury and the mercury jets was 1.5 ohms. The galvanometer used was one of the THOMSON-type, made by CARPENTIER, in which the original astatic system had been replaced by a system according to DU BOIS-RUBENS, made by SIEMENS and HALSKE, suspended by a quartz fibre of 7μ. The coils had a resistance of 2.7 ohms; the scale-distance was 2.8 metres; the magnifying power of the reading telescope was 33 times.

By adjusting the directing magnet the sensitiveness was raised to a deflection of 1 mm for 5.8×10^{-9} ampère; the total resistance being 4.2 ohms, 1 microvolt produced a deflection of 41 mm. With this sensitiveness, however, we could not make any measurements till after the cessation of the tramway traffic, but then we could trust the reading to within 0.1 mm, unless unusually large fluctuations of the magnetic declination occurred.

One of the apparatus ABC was attached to a solid stand permitting slow displacements in three perpendicular directions.

In order to collect the mercury the nozzles were placed in a short vertical glass tube of 4 cm. diameter, two vertical slots allowing

the tubes B to enter. The top of this tube was covered by a wooden ring with a glass window, through which the jets could be observed with the aid of a binocular microscope magnifying 15 times. The jets hit the glass window and the mercury dropped in a beaker placed underneath.

With suitable nozzles the first centimetres of the mercury jets appeared like highly polished metal wires, their diameters being capable of exact measurement on a divided scale in the eyepiece of the microscope.

In the experiments to be mentioned these diameters were 0.10 and 0.13 mm. Farther away from the orifices the surface of the jets was dull, an indication that they had broken up into droplets.

If the adjustable jet was slowly made to approach the other one, the surfaces came into contact, causing the jets to deviate from their original directions, which were perpendicular to each other. A slight displacement wholly changed the aspect: the jets united to a thin membrane, which resolved into droplets after a short distance. With central impact this membrane was perpendicular to the plane of the jets.

The upper part of tube B was surrounded over a length of 16 cm. by a close-fitting copper tube which could be heated by putting a gasburner under it. In this way the flowing mercury could reach a very high temperature. This was evidenced when once the pressure was released immediately after removing the flame, the glass tube being shattered by the sudden abundant development of vapour from the superheated liquid. An exact determination of the temperature seemed superfluous as the experiments were of a tentative character, so we simply estimated it from the aspect of the vapours rising from the jets.

Many series of observations were made on different days, which agreed perfectly with each other. The following table gives one of these as an example. The numbers in the second and third columns are scale readings in mm.

From $1^h 27^m$ to $1^h 31^m$ the jets were not heated, and readings were taken alternately with the jets not colliding and colliding centrally. The deflection is caused by spurious thermoforces in the circuit.

After that the gasflame was put under the copper tube, which causing the mercury jet to rise gradually in temperature; the deflections increased at the same time. After the removal of the flame the deflections decreased, resuming the original value, as soon as the mercury had reached room-temperature. By heating the other tube

Time 6 March 1919.	Scale readings.		Deflection.
	Jets free.	Jets in contact.	
1ʰ 27ᵐ	154.2		
		161.9	+ 7.9
	153.8		
		161.9	+ 8.0
	154.0		
		161.7	+ 7.7
	154.0		
1ʰ 31ᵐ	flame under copper tube		
	153.2		
		161.4	+ 8.3
	153.0		
		161.7	+ 8.7
	153.0		
		162.0	+ 9.2
	152.5		
		162.6	+ 9.8
	153.0	vapours appear	
		163.0	+ 10.0
	153.0		
		163.2	+ 10.2
	153.0	abundant vapours	
		163.5	+ 10.8
	152.7		
		163.7	+ 10.8
	153.0		
	flame removed		
	152.7		
		163.5	+ 10.8
	152.7		
	mercury at room temperature		
	154.0		
		162.1	+ 8.0
1ʰ 41ᵐ	154.2		
1ʰ 48ᵐ	155.2		
		162.8	+ 7.6
	155.2		

the deflections became less than without heating, showing the effect to be reversible.

In order to find out whether the deflection for unequal temperatures of the jets — maximum 3.2 mm. — could be ascribed to a chemical reaction between the mercury and the glass, we heated tube B for an hour with the pressure off, so as to give some of

the mercury a much greater opportunity than in ordinary cases to form such a combination. Thus the mercury jet would have got different composition for the first minute of the experiment and a changed deflection would result. As we did not find any change in the deflection we cannot ascribe the observed effect to chemical contamination of the mercury.

Our effect may however be explained, as to magnitude and direction, by the thermo-electric force between mercury under pressure and mercury without pressure. This force was first observed by DES COUDRES [1]), and afterwards measured also by WAGNER and HÖRIG [2]). The mercury in our glass apparatus had the pressure of the compressed air, the mercury jets consisted of mercury at atmospheric pressure and their points of contact with the mercury at high pressure were at different temperatures.

We proved by a separate experiment that this explanation is the right one. We connected the tops of the tubes B by a short close-fitting glass knee, which was thus filled up by the mercury from the jets, a small aperture in the upper part serving as an overflow for the mercury. One of the tubes B now being heated, we obtained deflections of the same order as before, although there were no free mercury jets and therefore no sudden transition of temperature.

There is, however, one detail which remains unexplained in this way: we always found a greater effect for superficial contact of the jets than for a full contact. The difference increased with the difference in temperature and amounted to 15 mm. in maximo.

This phenomenon might be due to the increase of the temperature gradient at a superficial contact and then would prove the reality of BENEDICKS' so called fundamental effect. Of course one should not forget that this thermo-electric force amounts only to 3.5×10^{-8} Volt for the extremely steep fall of temperature of 300° over a distance less than 0.1 mm. Therefore this small force may be wholly neglected in all practical cases where it appears together with ordinary thermo-electric currents. We devised yet another experiment to demonstrate the minuteness — perhaps even the non-existence — of this effect of temperature fall, and to get rid of the disturbing pressure effect. A thin-walled glass tube was prepared, diameter outside 1.00 mm, inside 0.80 mm, and drawn down at the middle part to an outside diameter of 0.45 mm, inside diameter 0.30 mm. This tube was attached by short rubber tubes to the tubes B, from

[1]) DES COUDRES. Wied. Ann. **43**, p. 673, 1891.
[2]) E. WAGNER. Ann. d. Physik. **27**, p. 955, 1908.
   H. HÖRIG, Ann. d. Physik **28**, p. 871 1909.

which the narrow tops had been cut off. A small difference of level on the two sides then sufficed to draw a slow current of mercury through the thin tube. Without this current we could not detect any deflection when the small tube was heated on either side of the constriction. Now the section of the mercury in the tube was 0.50 mm², of the glass walls 0.38 mm², and in the constriction 0.08 mm² and 0.10 mm² respectively. The thermal conductivity of mercury being ten times that of glass, the conduction through the latter could not be of any moment here, as it was in BENEDICKS' experiment. Besides we could greatly increase the sensitiveness of our test by having the mercury streaming against the flow of heat. Thus the cold mercury streamed through the constriction and was heated immediately afterwards by a Bunsen flame, which surrounded the bare glass tube. In this way the walls of the constriction were certainly kept cool by the flow of mercury, the velocity of which was six times that in the heated tube. A temperature difference of 250° over a distance of a few millimetres was thus obtained. The galvanometer did not show the slightest deflection while 0.1 mm could have been detected with certainty, the zero being extremely steady in this case. Therefore any effect caused by the temperature gradient mentioned should be less than 1.10^{-9} Volt.

The above mentioned difference of 1.5 mm for different kinds of contact of the jets may very well be explained without the assumption of a thermo-electric force depending on the temperature gradient. From the quantity of mercury delivered per minute and the diameter of the jet we found its velocity to be 5 metres per second. Therefore the time of contact of the jets was of the order of 10^{-5} sec., and a small part of the mercury is cooled in this short time from 300° to half this value. It may well be that in this mercury the internal equilibrium between the electrons and the metal is upset, which would cause it to behave thermo-electrically like a different substance. As this different substance would have unequal temperatures at the two ends, a thermo-electric current would be produced.

In our opinion this investigation therefore disproves the existence of an effect as described by BENEDICKS, and there is accordingly no ground for modifying the existing theory of thermo-electricity.

Physical Laboratory University Groningen.

Mathematics. — "*On integral equations connected with differential equations*. By J. Droste. (Communicated by Prof. J. C. Kluyver).

(Communicated in the meeting of March 29, 1919).

§ 1. As is shown by Hilbert in his second paper on integral equations (Gött. Nachr. 1904, p. 213 sq.) there exists a connection between linear integral equations with symmetrical kernel and linear differential equations of the second order with linear homogeneous conditions between φ and $\dfrac{d\varphi}{dx}$ at the ends of the interval. Taking e.g. in the interval $(0,1)$ the equation

$$\frac{d^2\varphi}{dx^2} + \mu\varphi = 0, \qquad \ldots \ldots \ldots \quad (1)$$

μ being a constant, it may asked to determine the function $\varphi(x)$ so as to satisfy the differential equation and a condition at both ends of $(0,1)$. This is only possible for certain values of μ, the socalled characteristic numbers. Having chosen a value μ_0, for which the problem fails to have a solution, it will on the contrary be possible to find a symmetrical function $K(x,y)$, which, as a function of x, satisfies the differential equation and the conditions at the ends of the interval and which moreover has its derivative $\dfrac{\partial K(x,y)}{\partial x}$ disconti-nuous for $x = y$. The characteristic numbers and functions of the kernel $K(x,y)$ (being the numbers μ and the functions $\varphi(x)$, for which the equation

$$\varphi(x) = \mu \int_0^1 K(x,y)\,\varphi(y)dy \qquad \ldots \ldots \ldots \quad (2)$$

is valid) are the same values of μ and the same functions $\varphi(x)$ that solve the problem of the differential equation.

It appears, that the kernels considered above, viz. those satisfying the differential equation, are not the only ones to have $\varphi(x)$ for their characteristic functions. For the purpose of the reduction of the problem of the differential equation to another problem it is unnecessary to consider other kernels. But when an integral equation is given, it may be useful to have a method that enables us to know whether the kernel has or has not for its characteristic functions solutions

of (1) for certain values of μ. It therefore seems to me to be of some importance to consider generally the kernels the characteristic functions of which satisfy (1). From the examples of § 2 and § 3, containing two arbitrary functions, it will appear that very general classes of kernels have solutions of (1) for their characteristic functions.

§ 2. For $0 \leq x \leq 1$ and $0 \leq y \leq 1$

$$K(x,y) = F(x+y) + \Phi(x-y). \quad . \quad . \quad . \quad . \quad (2a)$$

will be a symmetrical function of x and y under the condition $\Phi(x-y) = \Phi(y-x)$. The function $F(z)$ has to be defined in the interval $(0,1)$, the function $\Phi(x)$ in the interval $(-1, +1)$. We suppose $F(z)$ and $\Phi(z)$ to have for $0 \leq z \leq 1$ the properties expressed by

$$F(z+1) = F(z) \quad , \quad \Phi(z-1) = \Phi(z) . \quad . \quad . \quad . \quad (3)$$

Supposing the possibility of expanding $F(z)$ and $\Phi(z)$ in uniformly convergent FOURIER series, we have

$$F(z) = a_0 + \sum_{k=1}^{\infty} a_k \cos (2\pi kz - \alpha_k) \quad , \quad (0 \leq \alpha_k < \pi)$$

$$\Phi(z) = b_0 + \sum_{k=1}^{\infty} b_k \cos 2\pi kz,$$

because from $\Phi(-z) = \Phi(z)$ and $\Phi(z-1) = \Phi(z)$ it follows that

$$\Phi(z) = \Phi(1-z).$$

Thus

$$K(x,y) = a_0 + \sum_{k=1}^{\infty} a_k \{\cos (2\pi kx - \tfrac{1}{2}\alpha_k) \cos (2\pi ky - \tfrac{1}{2}\alpha_k) -$$

$$- \sin (2\pi kx - \tfrac{1}{2}\alpha_k) \sin (2\pi ky - \tfrac{1}{2}\alpha_k)\}$$

$$+ b_0 + \sum_{k=1}^{\infty} b_k \{\cos (2\pi kx - \tfrac{1}{2}\alpha_k) \cos (2\pi ky - \tfrac{1}{2}\alpha_k) +$$

$$+ \sin (2\pi kx - \tfrac{1}{2}\alpha_k) \sin (2\pi ky - \tfrac{1}{2}\alpha_k)\}$$

$$= (b_0 + a_0) + \sum_{k=1}^{\infty} \{(b_k + a_k) \cos (2\pi kx - \tfrac{1}{2}\alpha_k) \cos (2\pi ky - \tfrac{1}{2}\alpha_k) +$$

$$+ (b_k - a_k) \sin (2\pi kx - \tfrac{1}{2}\alpha_k) \sin (2\pi ky - \tfrac{1}{2}\alpha_k)\}.$$

The functions

$$1 \quad , \quad \sqrt{2} \cos (2\pi ky - \tfrac{1}{2}\alpha_k) \quad , \quad \sqrt{2} \sin (2\pi ky - \tfrac{1}{2}\alpha_k) \quad . \quad . \quad (4$$

being orthogonal and normalised and the series converging uniformly, it follows by multiplying by one of those functions and integrating with respect to y from 0 to 1, that the functions (4) will be characteristic functions belonging to the characteristic numbers $1/(b_0 + a_0)$, $2/(b_k + a_k)$ and $2/(b_k - a_k)$. As a further characteristic function of $K(x,y)$ should have to be continuous and orthogonal to the system (4), it appears that such a function does not exist, the system (4) being complete.

The supposition of $F(z)$ and $\Phi(z)$ being developable in uniformly

convergent FOURIER series is unnecessary, as appears from another arrangement of the proof. Suppose $F(z)$ and $\Phi(z)$ to be continuous functions satisfying only the functional equations (3) and the equation $\Phi(-z) = \Phi(z)$. Then

$$\int_0^1 F(x+y) \cos\left(2\pi ky - \tfrac{1}{2}\alpha_k\right) dy = \int_x^{1+x} F(\xi) \cos\left(2\pi k\xi - 2\pi kx - \tfrac{1}{2}\alpha_k\right) d\xi.$$

The integrand having the period 1, it is allowed to integrate from 0 to 1 instead of from x to $x+1$. This gives

$$\int_0^1 F(x+y) \cos\left(2\pi ky - \tfrac{1}{2}\alpha_k\right) dy = \int_0^1 F(\xi) \cos\left(2\pi k\xi - 2\pi kx - \tfrac{1}{2}\alpha_k\right) d\xi$$

$$= \cos\left(2\pi kx + \tfrac{1}{2}\alpha_k\right) \int_0^1 F(\xi) \cos\left(2\pi k\xi\right) d\xi + \sin\left(2\pi kx + \tfrac{1}{2}\alpha_k\right) \int_0^1 F(\xi) \sin\left(2\pi k\xi\right) d\xi.$$

Now, if

$$a_0 + \sum_{k=1}^{\infty} a_k \cos\left(2\pi kz - \alpha_k\right)$$

be the FOURIER series of $F(z)$ (no supposition is made on the convergence), we have

$$\int_0^1 F(\xi) \cos\left(2\pi k\xi\right) d\xi = \tfrac{1}{2} a_k \cos \alpha_k, \qquad \int_0^1 F(\xi) \sin\left(2\pi k\xi\right) d\xi = \tfrac{1}{2} a_k \sin \alpha_k$$

and with this definition of α_k and a_k we have

$$\int_0^1 F(x+y)\cos\left(2\pi ky - \tfrac{1}{2}\alpha_k\right) dy =$$

$$= \tfrac{1}{2} a_k \cos\alpha_k \cos\left(2\pi kx + \tfrac{1}{2}\alpha_k\right) + \tfrac{1}{2} a_k \sin\alpha_k \sin\left(2\pi kx + \tfrac{1}{2}\alpha_k\right) = \tfrac{1}{2} a_k \cos\left(2\pi kx - \tfrac{1}{2}\alpha_k\right).$$

Suppose further

$$b_0 + \sum_{k=1}^{\infty} b_k \cos\left(2\pi kz\right)$$

to be the FOURIER series of $\Phi(z)$, i.e.

$$\int_0^1 \Phi(\xi) \cos\left(2\pi k\xi\right) d\xi = \tfrac{1}{2} b_k \quad, \quad \int_0^1 \Phi(\xi) \sin\left(2\pi k\xi\right) d\xi = 0.$$

Then, $\Phi(z)$ having the period 1,

$$\int_0^1 \Phi(x-y) \cos\left(2\pi ky - \tfrac{1}{2}\alpha_k\right) dy = \int_0^1 \Phi(\xi) \cos\left(2\pi k\xi + 2\pi kx - \tfrac{1}{2}\alpha_k\right) d\xi$$

$$= \tfrac{1}{2} b_k \cos (2\pi kx - \tfrac{1}{2}\alpha_k).$$

Therefore

$$\int_0^1 K(x,y) \cos (2\pi ky - \tfrac{1}{2}\alpha_k) dy = \tfrac{1}{2}(b_k + a_k) \cos (2\pi kx - \tfrac{1}{2}\alpha_k).$$

In the same way we may prove $\sin (2\pi kx - \tfrac{1}{2}\alpha_k)$ to be a characteristic function (that 1 is such a function appears at once). Of course some of the functions (4) may be absent from the set of characteristic functions of $K(x,y)$, viz. in the case the corresponding value of $a_0 + b_0$ or $a_k + b_k$ or $b_k - a_k$ be zero.

§ 3. $K(x,y)$ be a kernel of the form

$$K(x,y) = f(x+y) + \varphi(x-y), \quad \cdots \cdots \quad (5)$$

$f(z)$ being defined in $(0,2)$, $\varphi(z)$ in $(-1, +1)$.

We suppose again $\varphi(-z) = \varphi(z)$, so that $K(x,y)$ becomes symmetrical; we further suppose as before $f(z)$ and $\varphi(z)$ to be continuous. But now we make an assumption different from (3), viz.

$$f(z+1) = -f(z) \quad , \quad \varphi(z-1) = -\varphi(z) \quad \cdots \quad (6)$$

for $0 \leq z \leq 1$.

The functions

$$\sqrt{2} \cos \{(2k-1)\pi z - \tfrac{1}{2}\beta_k\} \quad , \quad \sqrt{2} \sin \{(2k-1)\pi z - \tfrac{1}{2}\beta_k\} \quad \cdots \quad (7)$$

for $k = 1, 2, \ldots$ form a system of normalized orthogonal functions for all values of β_k. Now

$$\int_0^1 f(x+y) \cos\{(2k-1)\pi y - \tfrac{1}{2}\beta_k\} dy = \int_x^{1+x} f(\xi) \cos\{(2k-1)\pi\xi - (2k-1)\pi x - \tfrac{1}{2}\beta_k\} d\xi.$$

If we divide the integral into three parts, one integral from 0 to 1, another from 1 to x and a third from 0 to x (the latter with the negative sign) and make in the second integral the substitution $\xi = 1 + \xi_1$, that integral becomes

$$- \int^x f(1+\xi_1) \cos \{(2k-1)\pi\xi_1 - (2k-1)\pi x - \tfrac{1}{2}\beta_k\} d\xi_1$$

so that it cancels the third integral. We thus have

$$\int_0^1 f(x+y) \cos\{(2k-1)\pi y - \tfrac{1}{2}\beta_k\} dy = \int_0^1 f(\xi)\cos\{(2k-1)\pi\xi - (2k-1)\pi x - \tfrac{1}{2}\beta_k\} d\xi$$

$$= \cos \{(2k-1)\pi x + \tfrac{1}{2}\beta_k\} \int_0^1 f(\xi)\cos(2k-1)\pi\xi d\xi +$$

$$+ \sin\{(2k-1)\pi x + \tfrac{1}{2}\beta_k\} \int_0^1 f(\xi)\sin(2k-1)\pi\xi d\xi = \tfrac{1}{2}c_k \cos\{(2k-1)\pi x - \tfrac{1}{2}\beta_k\},$$

putting

$$\int_0^1 f(\xi)\cos(2k-1)\pi\xi d\xi = \tfrac{1}{2}c_k \cos\beta_k \quad , \quad \int_0^1 f(\xi)\sin(2k-1)\pi\xi d\xi = \tfrac{1}{2}c_k \sin\beta_k,$$

by which β_k and c_k are defined. We take $0 \leqq \beta_k \leqq \pi$.

In the same way

$$\int_0^1 f(x+y)\sin\{(2k-1)\pi y - \tfrac{1}{2}\beta_k\}dy = \int_0^1 f(\xi)\sin\{(2k-1)\pi\xi - (2k-1)\pi x - \tfrac{1}{2}\beta_k\}d\xi$$

$$= - \sin\{(2k-1)\pi x + \tfrac{1}{2}\beta_k\} \int_0^1 f(\xi)\cos(2k-1)\pi\xi d\xi +$$

$$+ \cos\{(2k-1)\pi x + \tfrac{1}{2}\beta_k\} \int_0^1 f(\xi)\sin(2k-1)\pi\xi d\xi = - \tfrac{1}{2}c_k \sin\{(2k-1)\pi x - \tfrac{1}{2}\beta_k\}.$$

Further

$$\int_0^1 \varphi(x-y)\cos\{(2k-1)\pi y - \tfrac{1}{2}\beta_k\}dy = \int_{-x}^{1-x} \varphi(\xi)\cos\{(2k-1)\pi\xi + (2k-1)\pi y - \tfrac{1}{2}\beta_k\}d\xi.$$

As again

$$\int_{-x}^0 \varphi(\xi)\cos\{(2k-1)\pi\xi + (2k-1)\pi x - \tfrac{1}{2}\beta_k\}d\xi = \int_{1-x}^1 \varphi(\xi)\cos\{(2k-1)\pi\xi + (2k-1)\pi x - \tfrac{1}{2}\beta_k\}d\xi$$

we have

$$\int_0^1 \varphi(x-y)\cos\{(2k-1)\pi y - \tfrac{1}{2}\beta_k\}dy = \int_0^1 \varphi(\xi)\cos\{2k-1)\pi\xi + (2k-1)\pi x - \tfrac{1}{2}\beta_k\}d\xi$$

$$= \tfrac{1}{2}d_k \cos\{(2k-1)\pi x - \tfrac{1}{2}\beta_k\},$$

putting

$$\int_0^1 \varphi(\xi)\cos(2k-1)\pi\xi d\zeta = \tfrac{1}{2}d_k,$$

where $\int_0^1 \varphi(\xi)\sin(2k-1)\pi\xi d\xi = 0$ from $\varphi(1-z) = -\varphi(z)$.

If in this formula we read $\frac{1}{2}\beta_k + \dfrac{\pi}{2}$ instead of $\frac{1}{2}\beta_k$, we get

$$\int_0^1 \varphi(x-y) \sin\{(2k-1)\pi y - \tfrac{1}{2}\beta_k\}dy = \tfrac{1}{2}d_k \sin\{(2k-1)\pi x - \tfrac{1}{2}\beta_k\}.$$

From these considerations it appears that

$$\int_0^1 K(x,y)\cos\{(2k-1)\pi y - \tfrac{1}{2}\beta_k\}dy = \tfrac{1}{2}(d_k+c_k)\cos\{2k-1)\pi x - \tfrac{1}{2}\beta_k\},$$

$$\int_0^1 K(x,y)\sin\{(2k-1)\pi y - \tfrac{1}{2}\beta_k\}dy = \tfrac{1}{2}(d_k-c_k)\sin\{(2k-1)\pi y - \tfrac{1}{2}\beta_k\}$$

and this proves, that the functions (7) are characteristic functions of $K(x,y)$ belonging to the characteristic numbers $2/(d_k + c_k)$ and $2/(d_k - c_k)$.

There exist no other characteristic functions, for the functions (7) form a complete system; so we have found the characteristic functions and numbers of the kernel (5).

Every symmetrical kernel of the form

$$K(x,y) = D(x+y) + \Delta(x-y)$$

is the sum of a kernel such as (2) and a kernel such as (5). For $D(z)$ and $\Delta(z)$ being defined in $(0,2)$ and $(-1,+1)$, one may put

$2F(z) = D(z) + D(1+z)$, $2f(z) = D(z) - D(1+z)$ for $0 \le z \le 1$,
$2F(z) = D(z) + D(z-1)$, $2f(z) = D(z) - D(z-1)$ for $1 \le z \le 2$,
$2\Phi(z) = \Delta(z) + \Delta(z+1)$, $2\varphi(z) = \Delta(z) - \Delta(z+1)$ for $-1 \le z \le 0$,
$2\Phi(z) = \Delta(z) + \Delta(z-1)$, $2\varphi(z) = \Delta(z) - \Delta(z-1)$ for $0 \le z \le 1$,

and so $K(x,y)$ becomes the sum of a kernel such as (2) and a kernel such as (5). But from this there is little to conclude with respect to the characteristic functions of $K(x,y)$.

§ 4. We now consider a much more general case. The equation

$$\frac{d}{dx}\left(p(x)\frac{dz}{dx}\right) + \{q(x) + \mu\}z = 0 \quad \ldots \ldots \quad (8)$$

be given; we put for brevity

$$\triangle_x z = \frac{d}{dx}\left(p(x)\frac{dz}{dx}\right) + q(x)z, \quad \ldots \ldots \quad (9)$$

so that the differential equation becomes

$$\triangle_x z + \mu z = 0 \quad \ldots \ldots \ldots \quad (8a)$$

We suppose the function $p(x)$ to have a continuous differential coefficient in the interval (a,b) and the function $q(x)$ to be continuous in that interval.

Further $K(x,y)$ be a symmetrical kernel for $a \leq x \leq b$ and $a \leq y \leq b$ and this kernel be two times continuously differentiable with respect to x (and of course also with respect to y). We assume the identity

$$\Delta_x K(x,y) = \Delta_y K(x,y) \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Then, $\psi(x)$ being a continuous function in (a,b), it appears that

$$\frac{d}{dx} \int_a^b K(x,y)\psi(y)dy = \int_a^b \frac{\partial K(x,y)}{\partial x} \psi(y)dy$$

and

$$\frac{d^2}{dx^2} \int_a^b K(x,y)\psi(y)dy = \int_a^b \frac{\partial^2 K(x,y)}{\partial x^2} \psi(y)dy,$$

as may be shown by means of integration of these equations with respect to x, as this integration, on the assumptions made, may be effected under the sign of integration. In the same way it appears, that every characteristic function $\varphi(x)$ of $K(x,y)$ may be differentiated twice.

We put

$$\Delta(x,y) = \left[p(\eta) \left\{ K(x,\eta) \frac{\partial K(\eta,y)}{\partial \eta} - \frac{\partial K(x,\eta)}{\partial \eta} K(\eta,y) \right\} \right]_a^b, \quad . \quad (11)$$

the sign of substitution relating, as always in the sequel, to η.

We now have the following

Theorem I. If $\varphi(x)$ be a characteristic function of $K(x,y)$, i.e. when

$$\varphi(x) = \lambda \int_a^b K(x,y)\varphi(y)dy, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

we have

$$\Delta_x \varphi(x) = \lambda \int_a^b K(x,y) \, \Delta_y \varphi(y)dy - \lambda^2 \int_a^b \Delta(x,y)\varphi(y)dy \quad . \quad . \quad (13)$$

Proof. We have

$$\Delta_x \varphi(x) = \lambda \int_a^b \Delta_x K(x,y) \, \varphi(y)dy = \lambda \int_a^b \{\Delta_y K(x,y)\} \, \varphi(y)dy$$

from (10). Now for two arbitrary, twice continuously differentiable, functions the so called formula of GREEN is valid; in the case of functions $K(x,y)$ and $\varphi(y)$ it takes the form

$$\int_a^b \{K(x,y)\Delta_y\varphi(y) - \varphi(y)\Delta_y K(x,y)\}dy = \left[p(\eta) \left\{ K(x,\eta)\varphi'(\eta) - \frac{\partial K(x,\eta)}{\partial \eta} \varphi(\eta) \right\} \right]_a^b.$$

From this we find

$$\Delta_x \varphi(x) = \lambda \int_a^b K(x,y) \, \Delta_y \varphi(y) dy - \lambda \left[p(\eta) \left\{ K(x,\eta) \varphi'(\eta) - \frac{\partial K(x,\eta)}{\partial \eta} \varphi(\eta) \right\} \right]_a^b.$$

Substituting in this equation

$$\varphi(\eta) = \lambda \int_a^b K(\eta,y) \varphi(y) dy,$$

$$\varphi'(\eta) = \lambda \int_a^b \frac{\partial K(\eta,y)}{\partial \eta} \varphi(y) dy,$$

we get (13).

Theorem II. The necessary and sufficient condition that a complete system of orthogonal characteristic functions of $K(x,y)$ be solutions of (8), *is that $K(x,y)$ satisfies identically in x and y the equation*

$$\Delta(x,y) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Proof. First we assume $\Delta(x,y) = 0$. If then $\varphi(x)$ be a characteristic function belonging to the characteristic number λ, it follows from (13) that

$$\Delta_x \varphi(x) = \lambda \int_a^b K(x,y) \Delta_y \varphi(y) dy.$$

Consequently $\Delta_x \varphi(x)$ is a characteristic function for the number λ. Now if $\varphi_1(x), \ldots, \varphi_n(x)$ be a complete orthogonal and normalized system of characteristic functions all belonging to λ, the functions $\Delta_x \varphi_1(x), \ldots, \Delta_x \varphi_n(x)$ also will be characteristic functions for the value λ; consequently they are expressible in $\varphi_1(x), \ldots, \varphi_n(x)$ by formulae of the form

$$\Delta_x \varphi_i(x) = \sum_{j=1}^{n} c_{ij} \varphi_j(x) \quad . \quad . \quad . \quad . \quad . \quad (15)$$

From this

$$c_{ij} = \int_a^b \varphi_j(x) \Delta_x \varphi_i(x) dx.$$

The formula of GREEN now gives

$$c_{ij} - c_{ji} = \int_a^b \{\varphi_j(x)\Delta_x \varphi_i(x) - \varphi_i(x)\Delta_x \varphi_j(x)\} dx =$$

$$[p(\eta)\{\varphi_j(\eta)\varphi'_i(\eta) - \varphi_i(\eta)\varphi'_j(\eta)\}]_a^b$$

and if we substitute in this formula

$$\varphi_j(\eta) = \lambda \int_a^b K(x,\eta)\, \varphi_j(x)dx,$$

$$\varphi_j'(\eta) = \lambda \int_a^b \frac{\partial K(x,\eta)}{\partial \eta}\, \varphi_j(x)dx$$

and other analogous expressions for $\varphi_i(\eta)$ and $\varphi_i'(\eta)$, with y as the variable of integration, we get

$$c_{ij} - c_{ji} \quad \lambda^2 \int_a^b \int_a^b \left[p(\eta) \left\{ K(x,\eta) \frac{\partial K(\eta,y)}{\partial \eta} - \frac{\partial K(x,\eta)}{\partial \eta} K(\eta,y) \right\} \right]_a^b \varphi_j(x)\varphi_i(y)dxdy$$

$$= \lambda^2 \int_a^b \int_a^b \Delta(x,y)\varphi_j(x)\varphi_i(y)dxdy = 0.$$

This proves that $c_{ij} = c_{ji}$. By means of an orthogonal transformation it is always possible to find n other functions $\psi_1(x), \ldots, \psi_n(x)$, linearly expressed in $\varphi_1(x), \ldots, \varphi_n(x)$, orthogonal and normalized, but such, that instead of (15) they satisfy equations of the form

$$\Delta_x \psi_i(x) = -\mu_i \psi_i(x),$$

i.e. (8). This proves the condition $\Delta(x,y) = 0$ to be sufficient.

We now suppose that we know a complete system of orthogonal characteristic functions of $K(x,y)$ to consist of solutions of (8). If $\varphi_1(x), \ldots, \varphi_i(x), \ldots$ be that system and $\mu_1, \ldots, \mu_i, \ldots$ the corresponding values of μ, it follows from (12) and (13) that

$$\Delta_x \varphi_i(x) + \mu_i \varphi(x) = \lambda_i \int_a^b K(x,y) \{ \Delta_y \varphi_i(y) + \mu_i \varphi(y) \}\, dy - \lambda_i^2 \int_a^b \Delta(x,y)\varphi_i(y)\, dy$$

and so, as $\varphi_i(x)$ satisfies the differential equation,

$$\int_a^b \Delta(x,y)\, \varphi_i(y)\, dy = 0$$

for all values of i. Consequently $\Delta(x,y)$ is a function of y, that is orthogonal to all characteristic functions of $K(x,y)$ and this proves that

$$\int_a^b \Delta(x,y)\, K(y,z)\, dy = 0 \quad . \quad . \quad . \quad . \quad . \quad (16)$$

for all values of x and z in (a,b). From this we get

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$$\int_{a}^{b} \Delta\,(x,y)\,\frac{\partial K(y,z)}{\partial z}\,dy = 0 \quad . \quad . \quad . \quad . \quad . \quad (16a)$$

We now have

$$\int_{a}^{b} \{\Delta(x,y)\}^{2}dy = \int_{a}^{b}\Delta(x,y)\left[\,p(\eta)\left\{K(x,\eta)\,\frac{\partial K(\eta,y)}{\partial\eta} - \frac{\partial K(x,\eta)}{\partial\eta}\,K(\eta,y)\right\}\right]_{a}^{b}dy =$$

$$=\left[\,p(\eta)K(x,\eta)\int_{a}^{b}\Delta(x,y)\,\frac{\partial K(\eta,y)}{\partial\eta}\,dy\,\right]_{a}^{b} - \left[\,p(\eta)\,\frac{\partial K(x,\eta)}{\partial\eta}\int_{a}^{b}\Delta(x,y)K(\eta,y)dy\,\right]_{a}^{b}$$

and this becomes 0 in consequence of (16) and (16a). As $\Delta(x,y)$ is a continuous function of y, this proves it to be zero for all values of x and y in (a,b). Hence the condition is necessary.

Example. Put $\Delta_x = \dfrac{d^2}{dx^2}$. The kernel $K(x,y)$ will have the form

$$K(x,y) = F(x+y) + \Phi(x-y)$$

with $\Phi(x-y) = \Phi(y-x)$. We suppose $a = 0$, $b = 1$. We then get
$$\Delta(x,y) = (\{F(x+1) + \Phi(x-1)\}\{F''(y+1) - \Phi'(y-1)\} --$$
$$- \{F''(x+1) - \Phi'(x-1)\}\{F(y+1) + \Phi(y+1)\})$$
$$- (\{F'(x) + \Phi(x)\}\{F'(y)-\Phi'(y)\} - \{F''(x)-\Phi'(x)\}\{F(y) + \Phi(y)\})$$

In consequence of (3) $\Delta(x,y)$ becomes zero; if we suppose (6) to be satisfied (after substituting in that equation F for f and Φ for φ) the expression $\Delta(x,y)$ also becomes zero. In both cases the characteristic functions are solutions of (1), in agreement to what we have found in § 2 and § 3.

§ 5. We will now consider condition (14) more closely. Putting for brevity

$$\frac{\partial K(x,\eta)}{\partial\eta}\bigg|_{x=b} = P(x), \quad \frac{\partial K(x,\eta)}{\partial\eta}\bigg|_{x=a} = Q(x), \quad K(x,b) = S(x) \quad K(x,a) = T(x),$$

it becomes

$$p(b)\{S(x)\,P(y) - P(x)\,S(y)\} = p(a)\{T(x)\,Q(y) - Q(x)\,T(y)\} \quad . \quad . \quad (14a)$$

We first suppose $p(b) \neq 0$, $p(a) \neq 0$ and we assume the existence of two values y_1 and y_2 in (a,b), for which $S(y_1)\,P(y_2) - S(y_2)\,P(y_1) \neq 0$. If for brevity we write P_1, etc., P_2, etc. instead of $P(y_1)$, etc., $P(y_2)$, etc., equation (14a), after substitution of y_1 and y_2 for y, becomes
$$p(b)P_1S(x) - p(b)S_1P(x) = p(a)Q_1T(x) - p(a)T_1Q(x),$$
$$p(b)P_2S(x) - p(b)S_2P(x) = p(a)Q_2T(x) - p(a)T_2Q(x).$$

Eliminating $P(x)$ or $S(x)$ we get

$$p(b)\,(P_1S_2 - P_2S_1)\,S(x) = p(a)\,\{(Q_1S_2 - Q_2S_1)T(x) + (S_1T'_2 - S_2T_1)Q(x)\},$$
$$p(b)\,(P_1S_2 - P_2S_1)\,P(x) = p(a)\,\{(Q_1P_2 - Q_2P_1)T(x) + (P_1T'_2 - P_2T_1)Q(x)\}.$$

Putting now

$$\frac{p(a)}{p(b)}\frac{Q_1S_2 - Q_2S_1}{P_1S_2 - P_2S_1} = \alpha, \quad \frac{p(a)}{p(b)}\frac{S_1T_2 - S_2T_1}{P_1S_2 - P_2S_1} = \beta, \quad \frac{p(a)}{p(b)}\frac{Q_1P_2 - Q_2P_1}{P_1S_2 - P_2S_1} = \gamma,$$

$$\frac{p(a)}{p(b)}\frac{P_1T_2 - P_2T_1}{P_1S_2 - P_2S_1} = \delta,$$

we get

$$S(x) = \alpha T(x) + \beta Q(x),$$
$$P(x) = \gamma T(x) + \delta Q(x).$$

It is easy to verify the condition

$$p(b)\,(\alpha\delta - \beta\gamma) = p(a) \quad \ldots \quad \ldots \quad (17)$$

We thus see, that S and P may be calculated from T and Q by a linear substitution. Replacing these functions by what they mean, we have

$$K(x, b) = \alpha\,K(x,a) + \beta\,\frac{\partial K(x,\eta)}{\partial \eta}\bigg|_{\eta=a},$$

$$\frac{\partial K(x,\eta)}{\partial \eta}\bigg|_{\eta=b} = \gamma\,K(x,a) + \delta\,\frac{\partial K(x,\eta)}{\partial \eta}\bigg|_{\eta=a} \qquad \ldots \quad (18)$$

That, on the other hand, these equations satisfy (14) appears from the fact that in (18) the determinant of the left hand quantities for two values of x, say x and y, is equal to $(\alpha\delta - \beta\gamma)$ times the determinant of the quantities $K(x,a)$ and $\dfrac{\partial K(x,\eta)}{\partial \eta}\bigg|_{\eta=a}$ for the two values x and y; this shews, in connection with (17), that (14) is satisfied.

The inverse substitution of (18) is

$$K(x,a) = \alpha'\,K(x,b) + \beta'\,\frac{\partial K(x,\eta)}{\partial \eta}\bigg|_{\eta=b},$$

$$\frac{\partial K(x,\eta)}{\partial \eta}\bigg|_{\eta=a} = \gamma'\,K(x,b) + \delta'\,\frac{\partial K(x,\eta)}{\partial \eta}\bigg|_{\eta=b} \qquad \ldots \quad (18a)$$

with the condition

$$p(a)\,(\alpha'\delta' - \beta'\gamma') = p(b) \quad \ldots \quad \ldots \quad (17a)$$

If it be impossible to determine y_1 and y_2 so that $S_1P_2 - S_2P_1 \neq 0$, $S(x)$ and $P(x)$ will be proportional and from (14a) it is seen that in that case also $Q(x)$ and $T(x)$ will be proportional. This may also be considered as a consequence of (18).

In the case $p(a) = 0$, $p(b) \neq 0$ it follows from (14a) that $S(x)$ and $P(x)$ will be proportional and as then the proportionality of $S(x)$ and $P(x)$ is a consequence of (18) and (17a), it is allowed to

consider (18) as valid also in that case. In the same way (18a) is valid if $p(b) = 0$, and $p(a) \neq 0$.

If $p(a) = p(b) = 0$, a kernel for which the functions $P(x)$, $Q(x)$, $S(x)$ and $T(x)$ remain finite, will always satisfy (14) and so its characteristic functions will always be solutions of (8).

§ 6. From the conditions (18) for the kernel it is not difficult to get conditions for the characteristic functions. If $\varphi_i(x)$ be such a function we have

$$\varphi_i(x) = \lambda_i \int_a^b K(x,y)\varphi_i(y)dy,$$

and so

$$\varphi'_i(x) = \lambda_i \int_a^b \frac{\partial K(x,y)}{\partial x} \varphi_i(y)dy$$

Hence

$$\varphi_i(a) = \lambda_i \int_a^b K(y,a)\varphi_i(y)dy \quad , \quad \varphi'_i(a) = \lambda_i \int_a^b \frac{\partial K(y,\eta)}{\partial \eta}\bigg|_{\eta=a} \varphi_i(y)dy,$$

$$\varphi_i(b) = \lambda_i \int_a^b K(y,b)\varphi_i(y)dy \quad , \quad \varphi'_i(b) = \lambda_i \int_a^b \frac{\partial K(y,\eta)}{\partial \eta}\bigg|_{\eta=b} \varphi_i(y)dy.$$

From (18) we now get

$$\left.\begin{array}{l} \varphi_i(b) = \alpha\varphi_i(a) + \beta\varphi'_i(a), \\ \varphi'_i(b) = \gamma\varphi_i(a) + \delta\varphi'_i(a). \end{array}\right\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (19)$$

§ 7. To conclude, we will find the conditions (19) for the orthogonality of the solutions of (18) in a direct way, independent of a kernel whatever. We suppose $\varphi(x)$ and $\psi(x)$ to be two solutions of (8):

$$\Delta_x\varphi(x) + \mu_1\varphi(x) = 0,$$
$$\Delta_y\psi(x) + \mu_2\psi(x) = 0.$$

Multiplying the former of these equations by $\psi(x)$, the latter by $\varphi(x)$ and subtracting we find

$$\frac{d}{dx}[p(x)\{\psi(x)\varphi'(x) - \varphi(x)\psi'(x)\}] + (\mu_1 - \mu_2)\varphi(x)\psi(x) = 0$$

and from this

$$[p(\eta)\{\varphi(\eta)\psi'(\eta) - \psi(\eta)\varphi'(\eta)\}]_a^b = (\mu_1 - \mu_2)\int_a^b \varphi(x)\psi(x)dx.$$

If φ and ψ correspond to different values of μ we see that for the orthogonality it is necessary and sufficient that

$$\left[p(\eta)\{\varphi(\eta)\psi'(\eta)-\psi(\eta)\varphi'(\eta)\} \right]_a^b = 0 \quad \ldots \quad (20)$$

If φ and ψ correspond to the same μ the condition will be necessary. So $\varphi_1(x),\varphi_2(x),\ldots$ being an orthogonal system, (19) must be valid for every pair of functions of the system.

Putting generally

$$\varphi_i(a) = x_i \quad , \quad \varphi'_i(a) = y_i \quad , \quad \varphi_i(b) = u_i \quad , \quad \varphi'_i(b) = v_i,$$

we get from (19)

$$p(a)\,(x_i y_j - x_j y_i) = p(b)\,(u_i v_j - u_j v_i)$$

for every pair of indices i and j. For the three indices i, r and s the equations become

$$p(a)\,(x_i y_r - x_r y_i) = p(b)(u_i v_r - u_r v_i)$$
$$p(a)\,(x_r y_s - x_s y_r) = p(b)\,(u_r v_s - u_s v_r),$$
$$p(a)\,(x_s y_i - x_i y_s) = p(b)\,(u_s v_i - u_i v_s).$$

Multiplying the first of these equations by u_s, the second by u_i, the third by u_r and adding we get

$$p(a) \begin{vmatrix} u_i & x_i & y_i \\ u_r & x_r & y_r \\ u_s & x_s & y_s \end{vmatrix} = 0$$

In the same way, multiplying by v_s, v_i, v_r we get

$$p(a) \begin{vmatrix} v_i & x_i & y_i \\ v_r & x_r & y_r \\ v_s & x_s & y_s \end{vmatrix} = 0$$

So, if $p(a) \neq 0$, it follows from this, by expanding the determinant with respect to the elements of the first row,

$$u_i(x_r y_s - x_s y_r) + x_i(y_r u_s - y_s u_r) + y_i(u_r x_s - u_s x_r) = 0,$$
$$v_i(x_r y_s - x_s y_r) + x_i(y_r v_s - y_s v_r) + y_i(v_r x_s - v_s x_r) = 0.$$

We now choose the indices r and s so that $x_r y_s - x_s y_r \neq 0$. Then putting

$$\frac{y_s u_r - y_r u_s}{x_r y_s - x_s y_r} = \alpha, \quad \frac{u_s x_r - u_r x_s}{x_r y_s - x_s y_r} = \beta, \quad \frac{y_s v_r - y_r v_s}{x_r y_s - x_s y_r} = \gamma, \quad \frac{v_s x_r - v_r x_s}{x_r y_s - x_s y_r} = \delta,$$

we get for every value of i

$$u_i = \alpha x_i + b y_i,$$
$$v_i = \gamma x_i + \delta y_i.$$

It is easy to verify that

$$(\alpha\delta - \beta\gamma)\,(x_r y_s - x_s y_r) = u_r v_s - u_s v_r$$

and so

$$p(b)\,(\alpha\delta - \beta\gamma) = p(a) \quad \ldots \ldots \quad (21)$$

We have so found the formulae

$$\begin{aligned}\varphi_i(b) &= \alpha\varphi_i(a) + \beta\varphi_i'(a),\\ \varphi_i'(b) &= \gamma\varphi_i(a) + \delta\varphi_i'(a)\end{aligned} \quad \ldots \ldots \quad (19)$$

It is easy to verify by the aid of (21) that (19) satisfies (20).

If for every r and s the expression $x_r y_s - x_s y_r$ be zero, y_i and x_i will be proportional and then this will also be the case with u_i and v_i as is seen from (20).

If $p(a) = 0$ and $p(b) \neq 0$ we see from (21) that $\alpha\delta - \beta\gamma = 0$ and (19) that $\varphi_i(b)$ is proportional to $\varphi_i'(b)$; this satisfies (20) so that in that case (19) and (21) remain valid.

If $p(b) = 0$, $p(a) \neq 0$ the inverse substitution of (19), viz.

$$\begin{aligned}\varphi_i(a) &= \alpha'\varphi_i(b) + \beta'\varphi_i'(b),\\ \varphi_i'(a) &= \gamma'\varphi_i(b) + \gamma'\varphi_i'(b)\end{aligned} \quad \ldots \ldots \quad (19a)$$

with

$$p(a)\,(\alpha'\delta' - \beta'\gamma') = p(b), \quad \ldots \ldots \quad (21a)$$

shows that $\alpha'\delta' - \beta'\gamma' = 0$ and that, in connection with (21a), the quantities $\varphi_i(a)$ and $\varphi_i'(a)$ are proportional. This also follows from (20) and so we see that (19) and (19a) remain valid.

For $p(a) = p(b) = 0$ equation (20) is satisfied by all functions $\varphi_i(x)$, that remain finite in a and b.

Physics. — *"On the Theory of the Friction of Liquids* II.*"* By Prof. J. D. van der Waals Jr. (Communicated by Prof. J. D. van der Waals).

§ 4. *Distribution of density in a liquid flowing in a field of forces.* Before proceeding to the "friction by formation of groups", we shall discuss a simpler problem. We shall namely imagine that a gas streams in a field of force, and then examine what modifications are brought about by the streaming in the distribution of density as it would arise in a field of forces when there was no current. For this purpose we shall again imagine the simple case that the streaming takes place in the x-direction, and that the velocity may be represented by $u = az$. We shall further suppose that we have to do with a stationary current, so that in a point at rest in space the density and the velocity of the current are constant.

In order to examine the distribution of density which will present this stationary character, we shall assume that there are two causes that might give rise to a change in the density in a given point: the "molar" current, and the "diffusion" current. It is not to be denied that this distinction is artificial, and that the change of the quantity of substance in an element of space can of course always be found from the total current that flows in through the boundary surfaces. I shall, however, suppose that this total current may be thought composed of a molar current, to which I shall assign the unmodified velocity $u = az$, and a current which is the consequence of the inhomogeneous density in connection with the heat motion. The latter will be denoted by the name of diffusion current. I shall further assume that the change brought about by each of these two causes, can be computed independent of the other cause.

The quantity which enters a volume element per second through the molar current is:

$$\frac{dn}{dt}\, dx\, dy\, dz = -u\, \frac{\partial n}{\partial x}\, dx\, dy\, dz \quad . \quad . \quad . \quad . \quad (10)$$

In order to calculate the contribution of the diffusion current we shall assume that the distribution of the velocities of the gas-mole-

cules at any point may be found in the following way. We shall, namely, assume the velocities of the molecules which have collided in a certain layer to consist of two components: 1. the velocity of current in the layer in which they have collided, and 2 the heat motion, of which latter it will be assumed that it is distributed over the different molecules according to Maxwell's law. Undoubtedly we make an error when supposing these things, but we may expect that this will only be an error in a numerical coefficient, and that the nature of the phenomenon and also the order of magnitude will be correctly represented by the formulae derived by the aid of these suppositions.

In order to examine the diffusion current through a plane A, we shall consider two planes lying on either side of the plane A at a distance $\dfrac{\sqrt{3}}{3} l$. ($l =$ mean length of path of the molecules). And we shall consider the molecules passing through the plane A as "emitted" from one of these two planes, by which we understand that they have had their last collision there. Let us first consider the molecules that collide in the $+$ plane [1]), and which possess a component of velocity normal to the plane A between w and $w + dw$. Arrived in the plane A these molecules have obtained a normal velocity w' determined by the equation:

$$\tfrac{1}{2} m w'^2 = \tfrac{1}{2} m w^2 + \frac{\partial \varepsilon}{\partial z} \frac{l\sqrt{3}}{3}.$$

The number of molecules of this group passing per second and per unit of area through plane A, is when n represents the density of the molecules in A, and $n + \dfrac{\partial n}{\partial z} \dfrac{l\sqrt{3}}{3}$ that in the $+$ plane:

$$\frac{1}{\sqrt{\pi}^3} \left(n + \frac{\partial n}{\partial z} \frac{l\sqrt{3}}{3} \right) w' e^{-\frac{u^2+v^2+w'^2}{\alpha^2} + \frac{1}{kT}\frac{\partial \varepsilon}{\partial z}\frac{l\sqrt{3}}{3}} d\frac{u}{\alpha} d\frac{v}{\alpha} d\frac{w'}{\alpha} . \quad . \quad (11)$$

When we pay only attention to the molecules emitted from the $+$ plane, w' must always have a value for which $\tfrac{1}{2} m w'^2$ is $> \dfrac{\partial \varepsilon}{\partial z} \dfrac{l\sqrt{3}}{3}$. In the direction from $+$ to $-$ however, there go, also molecules

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[1]) i. e. the plane parallel to A at a distance $\tfrac{1}{3} l\sqrt{3}$ on the side where the potential energy ε of the molecules is greater than in A. The plane lying on the other side will be called the $-$ plane. The z-axis will be normal to A in the direction from the $-$ plane to the $+$ plane, so that $\dfrac{\partial \varepsilon}{\partial z} > 0$.

which have first passed through it in opposite direction with such a small velocity that they could not reach the + plane, but reversed their velocity in consequence of the force $-\dfrac{\partial \varepsilon}{\partial z}$ before having reached it. When also these molecules are taken into account the total diffusion current from + to — is found by integrating expression (11) with respect to u and v between $-\infty$ and $+\infty$ and with respect to w' between 0 and $-\infty$.

The molecules flowing in opposite i.e. in the + direction through the plane are found by taking a group of molecules emitted from the — plane:

$$\frac{1}{\sqrt{\pi^3}}\left(n - \frac{\partial n}{\partial z}\frac{l\sqrt{3}}{3}\right)w'e^{-\frac{u^2+v^2+w'^2}{\alpha^2}-\frac{1}{kT}\frac{\partial \varepsilon}{\partial z}\frac{l\sqrt{3}}{3}}d\frac{u}{\alpha}d\frac{v}{\alpha}d\frac{w'}{\alpha}$$

and by integrating u and v in this between $-\infty$ and $+\infty$ and w' between 0 and $+\infty$.

Thus it is found that the plane A is passed per second and per unit of area in the — direction by the following number of molecules:

$$\frac{\alpha}{2\sqrt{\pi}}\left\{\left(n + \frac{\partial n}{\partial z}\frac{l\sqrt{3}}{3}\right)e^{\frac{1}{kT}\frac{\partial \varepsilon}{\partial z}\frac{l\sqrt{3}}{3}} - \left(n - \frac{\partial n}{\partial z}\frac{l\sqrt{3}}{3}\right)e^{\frac{1}{kT}\frac{\partial \varepsilon}{\partial z}\frac{l\sqrt{3}}{3}}\right\} =$$

$$= \frac{\alpha\sqrt{3}}{3\sqrt{\pi}}l\left(\frac{\partial n}{\partial z} + n\frac{\partial \varepsilon}{\partial z}\frac{1}{kT}\right) = \frac{\alpha\sqrt{3}}{3\sqrt{\pi}}nl\left(\frac{1}{n}\frac{\partial n}{\partial z} + \frac{\partial \varepsilon}{\partial z}\frac{1}{kT}\right). \quad . \quad . \quad (12)$$

In this we shall assume nl to be constant, though, strictly speaking, this is only allowed for gases at small densities. In the case of thermodynamic equilibrium this diffusion current must be zero through very plane, so that then $l(n) + \dfrac{\varepsilon}{kT} =$ constant, which gives the known distribution of the molecules in space in that case.

We shall make use of the value of the diffusion current in equation (12) in order to calculate how much enters through the six sides of a volume element $dx\,dy\,dz$. We find for this:

$$-\frac{\alpha\sqrt{3}}{3\sqrt{\pi}}nl\,\nabla^2\left\{l(n) + \frac{\varepsilon}{kT}\right\}dx\,dy\,dz,$$

so that we find for the condition for a stationary state in connection with equation (10):

$$+\frac{\alpha\sqrt{3}}{3\sqrt{\pi}}nl\,\nabla^2\left\{l(n) + \frac{\varepsilon}{kT}\right\} = u\frac{\partial n}{\partial x} \quad . \quad . \quad . \quad (13)$$

I shall here leave out of account the question what corrections

would have to be applied to the numerical factor and use equation (13) further uncorrected.

$l(n) + \dfrac{\varepsilon}{kT}$ is the quantity that GIBBS represents by μ and denotes by the name of thermodynamic potential. In the case of thermodynamic equilibrium it is constant, and equal to $l(n_0)$, when n_0 is the density in the point where the potential energy is put zero. In the case of no equilibrium considered by us I shall put:

$$l(n) + \frac{\varepsilon}{kT} - l(n_0) = w. \qquad \ldots \ldots \ldots (14)$$

or taking into account that we suppose w to be small:

$$n = n_0 e^{-\frac{\varepsilon}{kT}}(1+w) = n_0 e^{-\frac{\varepsilon}{kT}} + nw, \qquad \ldots \ldots (14a)$$

so that nw represents the number of molecules that in consequence of the current is present in an element of space in excess above the normal number $n_0 e^{-\frac{\varepsilon}{kT}}$. According to equation (13) w is found as the potential of imaginary agent, of which the density would be: $-\dfrac{\sqrt{3\pi}}{a \cdot nl} u \dfrac{\partial n}{\partial x}$.

To illustrate the meaning of the found formula we shall apply it for the following simple case: the field of forces arises from a single centre of forces, in which we lay the origin O of the system of coordinates, the force being only a function of r. If there was no current, this field of forces would in a gas give rise to a denser cloud round O, in which the density would only be a function of r. Let us now think the gas set flowing with a *constant* velocity u in the negative x-direction, and let us suppose this to bring about a *slight* variation in the density, so that by way of first approximation we may take in equation (13) the value of $\dfrac{\partial n}{\partial x}$ as it would be without current, hence:

$$\frac{\partial n}{\partial x} = - n_0 e^{-\frac{\varepsilon}{kT}} \frac{1}{kT} \frac{\partial \varepsilon}{\partial x} \qquad \ldots \ldots \ldots (15)$$

which causes equation (13) to become:

$$\nabla^2 w = - \frac{\sqrt{3\pi}}{a \cdot nl} u \frac{n}{kT} \frac{\partial \varepsilon}{\partial x} \qquad \ldots \ldots \ldots (13a)$$

The imaginary agent is then negative on the side of the positive x-axis, and has an equal, but positive value on the side of the negative x-axis. Then the potential w of this agent will be zero in

the yz plane, as is easily derived from considerations of symmetry, and will on either side of it present the same sign as the imaginary agent. The excess nw, therefore, also shows these signs, which comes to this that the cloud has shifted in the direction of the negative x-axis, as was to be expected.

When we no longer assume u to be constant, but $u = az$, w will obtain a positive sign in the 1st and the 3rd quadrant, i.e. the cloud will be elongated in the direction of a line that forms an angle of 45° with the original axes and lies in the 1st and the 3rd quadrant.

§ 5. *Distribution of the density in a flowing liquid at the critical point.* When after these preparatory remarks we proceed to the problem of the anomalies of density in a flowing liquid, we shall first have to calculate $\nabla^2 w$ according to equation (13a). For this purpose we first remark that the value given for $\nabla^2 w$ by this equation is only a consequence of the movement of the gas relative to the centre of force. When we put $u = $ constant, and if we then make the centre of force participate in the movement, it would of course come to the same thing as if everything was at rest. We shall, therefore, always have to take this relative velocity for u in equation (13a). The value of $\nabla^2 w$ in a volume element $dx\,dy\,dz = d\omega$ can now be calculated as the sum of contributions furnished by forces exerted by the substance in the different surrounding volume elements. When we call one of these surrounding elements $dx'\,dy'\,dz' = d\omega'$ and the density in it n', then the $n'd\omega'$ molecules in it can be conceived as a centre of force. When we put again $u = az$, the velocity of the substance in $d\omega$ relative this centre will amount to $a\,(z-z')$. Let us further represent the potential energy of two molecules at a mutual distance r by $\varphi(r)$, the contribution to $\nabla^2 w$ in $d\omega$ which is owing to the substance in $d\omega'$ is then:

$$-\frac{\sqrt{3\pi}}{\alpha \cdot nl}\frac{n}{kT}a(z-z')\,n'd\omega'\,\frac{\partial\varphi(r')}{\partial r'}\frac{x-x'}{r'}$$

in which r' represents the distance of the spacial elements $d\omega$ and $d\omega'$. When we turn the axes 45° round the y-axis, and when we call the new axes ξ, η, ζ, we find for the total value of $\nabla^2 w$:

$$\nabla^2 w = -\frac{\sqrt{3\pi}}{\alpha l}\frac{a}{kT}\int n'\frac{\partial\varphi}{\partial r'}\frac{(\xi-\xi')^2-(\zeta-\zeta')^2}{2r'}\,d\omega' \quad . \quad . \quad . \quad (16)$$

This equation gives the distribution of the imaginary agent in space. We find from it for the value of w_1 in a volume element

$d\xi_1\,d\eta_1\,d\zeta_1 = d\omega_1$, when we represent the distance of an element $d\omega$ to $d\omega_1$ by r_1:

$$w_1 = + \frac{\sqrt{3\pi}}{\alpha l}\,\frac{a}{kT}\,\iint n'\,\frac{\partial\varphi}{\partial r'}\,\frac{(\xi-\xi')^2-(\zeta-\zeta')^2}{2r'}\,\frac{1}{r_1}\,d\omega'd\omega \quad . \quad (17)$$

If n' were constant, we should of course find $\nabla^2 w = o$ and $w = o$. If, however, in a definite region n' is greater than in the surrounding volume elements, then in a line parallel to the ξ-axis and passing through the centre of this region $\nabla^2 w$ will be negative, and in a line parallel to the ζ-axis positive. The imaginary agent and w have then opposite signs, so that here also the condensed group will be elongated in a direction forming an angle of 45° with the original axes.

§ 6. *The application of the virial relation.* In order to calculate the stress tensor from the value found for w_1, we shall make use of the virial equation. We shall, however, have to demonstrate beforehand the applicability of this equation for the case under consideration. Let us for this purpose consider a definite volume in the space in which the flowing gas is found. We shall assign to it the shape of a rectangular parallelepiped and choose the coordinate axes parallel to the sides. As we think the state stationary, the expression $\Sigma\,m\,x\,\dot{x}$, in which the summation extends over all the molecules in the volume will be constant. The fact that through the boundary planes molecules enter and leave the considered space, does not affect this. We conclude from this that:

$$\frac{d}{dt}(\Sigma\,m\,x\,\dot{x}) = 0 = \Sigma\,m\,\dot{x}^2 + \Sigma\,x\,X + O\,m\,(x_1-x_2)\int\dot{x}^2 f(\dot{x})\,d\dot{x} \quad . \quad (18)$$

In this X is the x-component of the force acting on a molecule, x_1 and x_2 are the abscissae of the boundary planes of the parallelepiped normal to the x-axis, and O is the area of these planes. $f(\dot{x})\,d\dot{x}$ denotes the number of molecules per c.c.m²., of which the x-component of the velocity lies between $\dot{x}$ and $\dot{x}+d\dot{x}$. The latter term refers to the change in the value of $\Sigma\,m\,x\,\dot{x}$, which results from the molecules entering and leaving through the planes $x_1 = c$ and $x_2 = c$. The molecules entering and leaving through other boundary planes will yield on an average a contribution zero to $\frac{d}{dt}\Sigma\,m\,x\,\dot{x}$. Let us put:

$$\dot{x} = \dot{x}_{th} + u,$$

in which u represents the velocity of current and $\dot{x}_{th}$ the velocity of the heat motion, and let us take into consideration that

$$\Sigma\, 2\, m\, u\, \dot{x}_{th} = 0.$$

$$\int 2\, u\, \dot{x}_{th}\, f\,'(\dot{x})\, d\dot{x} = 0$$

and

$$\Sigma\, m\, u^2 + O\, m\, (x_1 - x_2)\, u^2 \int f(\dot{x})\, d\dot{x} = 0.$$

Equation (18) then assumes the following form :

$$\Sigma\, m\, \dot{x}^2{}_{th} + \Sigma\, x\, X + O\, (x_1 - x_2)\, m \int \dot{x}^2{}_{th}\, f(\dot{x})\, d\dot{x} = 0$$

Let us further split up X into X_1 and $\dot{X}_2$, in which X_1 refers to the mutual forces of the molecules in the considered volume and X_2 to the forces exerted by bodies lying outside the volume on the molecules contained in it. We shall only have to take forces X_2 into account that act in the planes $x_1 = c$ and $x_2 = c$; the others will be zero on an average. We shall further be allowed to put :

$$(\Sigma\, X_2)_{x_1} + m\, O \int \dot{x}_{th}{}^2\, f(\dot{x})\, d\dot{x} = p_{xx}\, O \quad . \quad . \quad . \quad . \quad (19)$$

in which $(\Sigma\, X_2)_{x_1}$ represents the sum of all the forces X_2 that act in the plane $x_1 = c$, and p_{xx} an element of the stress tensor in the well-known way. The lefthand member of (19), namely, indicates the total change of momentum which is caused by the substance on the lefthand side of the plane $x_1 = c$ in that on the righthand side both in consequence of transport by the molecules in their heat motion and in consequence of forces. As $O(x_2 - x_1) = V$ we find :

$$p_{xx}\, V = \Sigma\, m\, \dot{x}^2 + \Sigma\, x\, X_1$$

or

$$p_{xx} = \frac{RT}{V} - \Sigma'\, x\, X_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

when the sign Σ' in the last equation represents a summation over all the molecules in a c.c.m.

§ 7. *The stress tensor in a flowing liquid.* When we now calculate $p_{\xi\xi}$ according to equation (20), we find :

$$p_{\xi\xi} = \frac{RT}{V} - \iint \frac{\partial \varphi}{\partial r_{12}}\, n_1 n_2\, \frac{(\xi_2 - \xi_1)^2}{r_{12}}\, d\omega_1 d\omega_2, \quad . \quad . \quad (21)$$

in which $d\omega_1$ and $d\omega_2$ are two elements of space the distance of which is expressed by r_{12}, and in which the density of the molecules amounts respectively to n_1 and n_2. We now can put:

$$n_1 = \bar{n} + \Delta_1 + w_1(\bar{n} + \Delta_1)$$
$$n_2 = \bar{n} + \Delta_2 + w_2(\bar{n} + \Delta_2).$$

In this n represents the mean density, Δ the deviation, as we might expect it also without current, $w_1 n_1 = w_1 (n + \triangledown_1)$ representing according to § 4 the deviation from the mean density brought about by the current. Terms that would contain w^2, have been neglected. In the product $n_1 n_2$ the term $(\bar{n} + \Delta_1)(\bar{n} + \Delta_2)$ will yield the same value for all the coordinate directions. This term would also occur when there was no current, and its integral in equation (21) will produce the term $\dfrac{a}{v^2}$ of the hydrostatic pressure according to the equation of state. Let us also remark that $\overline{\bar{n}\Delta_1} = 0$ and $\overline{\bar{n}\Delta_2} = 0$, then (21) may be written as follows:

$$p_{\xi\xi} - p = -\iint_i \frac{\partial\varphi}{\partial r_{12}} \frac{(\xi_2 - \xi_1)^2}{r_{12}} (w_1 n_1 \Delta_2 + w_2 n_2 \Delta_1 + n_1 w_1 n_2 w_2) d\omega_1 \, d\omega_2 \quad (21a)$$

We shall neglect the third term. The 1st and the 2nd will be equal on an average, hence we may take twice the first. We shall substitute in it the value for w_1 that we have found in equation (17), in which we may replace n' by Δ', because when Δ' is everywhere zero, also w_1 becomes $= 0$. Thus we find:

$$p_{\xi\xi} - p = -\frac{\sqrt{3\pi}}{dl} \frac{a}{kT} \iiiint n_1 \Delta_2 \Delta' \frac{\partial\varphi}{\partial r'} \frac{(\xi - \xi')^2 - (\zeta - \zeta')^2}{r'}$$
$$\frac{1}{r_1} \frac{\partial\varphi}{\partial r_{12}} \frac{(\xi_2 - \xi_1)^2}{r_{12}} d\omega' d\omega \, d\omega_1 d\omega_2. \quad\quad\ldots\ldots (21b)$$

and in the same way:

$$p_{\zeta\zeta} - p = -\frac{\sqrt{3\pi}}{dl} \frac{a}{kT} \iiiint n_1 \Delta_2 \Delta' \frac{\partial\varphi}{\partial r'} \frac{(\xi - \xi')^2 - (\zeta - \zeta')^2}{r'}$$
$$\frac{1}{r_1} \frac{\partial\varphi}{\partial r_{12}} \frac{(\zeta_2 - \zeta_1)^2}{r_{12}} d\omega' d\omega \, d\omega_1 d\omega_2.$$

It will hardly be possible to calculate the value of these expressions accurately. I shall confine myself to a rough estimation of the order of magnitude, and demonstrate that $p_{\xi\xi} - p$ and $p_{\zeta\zeta} - p$ assume equal but opposed values, which in virtue of the properties of the stress tension had to be the case.

If for two different elements of space the values for Δ were always independent of each other, $\overline{\Delta_2 \Delta'}$ would be $= 0$, except when we make the element $d\omega'$ coincide with $d\omega_2$. When we then made the value of $d\omega_2$ approach zero, the righthand member of $(21b)$ would become zero. The Δ's for different elements of space are, however, not independent, but when Δ_2 is e.g. positive, the Δ's in the adjacent elements will probably also be positive, so that the product $\Delta_2 \Delta' d\omega_2 d\omega'$ will be positive on an average not only for $d\omega' = d\omega_2$, but also for a finite region round $d\omega_2$. In this region I shall assign to Δ' not only the same sign, but also the same value as to Δ_2, and I shall assume that the size of the region is equal to the sphere of attraction of a molecule [1]). I shall further assume that we get a sufficient approximation for $p_{\xi\xi} - p$, when we assign the value n to n_1, and I shall write ν for $\int n_1 \, d\omega'$, in which we extend the integration over the just-mentioned region. ν then represents the mean number of molecules in a sphere of attraction. At the critical density I should then be inclined to ascribe to ν a value between 5 and 25, though not much is to be said with certainty about this value. In consequence of these assumptions $(21b)$ passes into:

$$p_{\xi\xi} - p = - \frac{\sqrt{3\pi}}{a d} \frac{a\nu}{kT} \int\int\int \Delta_2^2 \frac{\partial\varphi}{\partial r_2} \frac{(\xi - \xi_2)^2 - (\zeta - \zeta_2)^2}{r_2} \cdot$$

$$\frac{1}{r_1} \frac{\partial\varphi}{\partial r_{12}} \frac{(\xi_2 - \xi_1)^2}{r_{12}} \, d\omega \, d\omega_1 d\omega_2 \quad . \quad . \quad . \quad . \quad (21c)$$

In order to find the sign of this expression, we transport the origin to the point $\zeta_2 \, \eta_2 \, \xi_2$, and first determine the sign of the quantity $\dfrac{\partial\varphi}{\partial r_2} \dfrac{(\xi - \xi_2)^2 - (\zeta - \zeta_2)^2}{r_2} \equiv Q$. The bisextrices of the angles between the displaced ξ and ζ-axes, divide the plane into four quadrants; two of them contain the ξ-axis, and two the ζ-axis. In the two quadrants that contain the ξ-axis, Q will be > 0, in the others Q will be < 0. If we next inquire into the sign of $\int Q \dfrac{1}{r_1} \, d\omega = I$, this sign will depend on the situation of the point $\xi_1 \, \eta_1 \, \zeta_1$.

If this point lies in the quadrants where $Q > 0$, I will also be

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[1]) Not improbably it is greater; but as the elements $d\omega'$ and $d\omega_2$, the mutual distance of which is much greater, do not appreciably contribute to the value of the righthand member of $(21b)$, the restriction to this value may be justified.

> 0 and vice versa. Let us now finally form $\int I\, \dfrac{\partial \varphi}{\partial r_{12}}\, \dfrac{(\xi_2 - \xi_1)^2}{r_{12}}\, d\omega_1$, and let us first integrate along a circle $r_{12} = $ constant; then the positive values of I will be multiplied by greater values of $(\xi_2 - \xi_1)^2$ than the negative values, so that the positive sign results. If we had calculated $p_{zz} - p$, we had multiplied by $(\zeta_2 - \zeta_1)^2$, so that then negative values of I had been multiplied by a greater factor, and the negative sign would have resulted.

In order to arrive at last at an estimation of the order of magnitude of $(p_{\xi\xi} - p)$, we observe that:

$$\int^{\cdot} \frac{\partial \varphi}{\partial r}\, r\, dx\, dy\, dz = \frac{\mathbf{a}}{N^2} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

in which $\mathbf{a}$ represents the known quantity $\mathbf{a}$ of the equation of state and N the number of molecules per molecular quantity.

We further assume that in the factor $\dfrac{1}{r_1}$ the radius of the sphere of attraction of the molecules (ϱ) may be written for r_1, and that the influence of the factors $\dfrac{(\xi - \xi_2)^2 - (\zeta - \zeta_2)^2}{r_2^2}$ and $\dfrac{(\xi_2 - \xi_1)^2}{r_{12}^2}$ will consist in this that the values which would be obtained by an omission of these factors, are multiplied by a moderate value μ, smaller than 1.

Thus we find, when we also take into account that $NkT = RT$:

$$p_{\xi\xi} - p = - \frac{a \sqrt{3\pi}}{d\, RT}\, r\mu\, \overline{\Delta^2}\, \frac{(\mathbf{a})^2}{N^3}\, \frac{1}{\varrho} \quad . \quad . \quad . \quad (21d)$$

If we had calculated p, we should also have found a term with Δ^2 in the virial of the attractive forces. If we call it p', then:

$$p' = \tfrac{1}{3}\, \Delta^2\, \frac{\mathbf{a}}{N^2}$$

so that:

$$\frac{p_{\xi\xi} - p}{p'} = - \frac{a \sqrt{3\pi}}{3a\, l\, RT}\, v\, \mu\, \frac{\mathbf{a}}{N}\, \frac{1}{\varrho} = \pm\, 10^{-11}.$$

As our purpose was only a rough estimation, we have taken in this:

$$a = 1 \qquad \text{and} \qquad r\mu = 1$$
$$a = 3.10^4$$
$$l = 10^{-7}$$
$$\varrho = 5.10^{-8}$$
$$N = 6.10^{23}$$

When we take for $p_k = 70$ atm. for CO_2 and $\eta = 0,000678$, we find:

$$\frac{\eta}{p} = \pm \, 10^{-11}$$

Now $p_k = $ round $\dfrac{1}{8} \dfrac{\mathbf{a}}{v_k{}^2}$ and $p' = \dfrac{\Delta^2}{n^2} \dfrac{\mathbf{a}}{v_k{}^2}$, hence if at the critical point the mean Δ becomes somewhat smaller, but of the same order of magnitude as $\overline{n}$, then $p_{zz} - p$ will become of the same order of magnitude as η for a gradient of velocity $a = 1$, and must, therefore, certainly, be taken into account. On the strength of this we should have to expect that an abnormally great value of η would be found at the critical density, when for T'_k we examined the value η as function of the density. WARBURG and VON BABO [1] have determined η for CO_2 at $32,6°$ for different densities. η increases with the density. There does not appear any irregular increase at the critical density from their observations. It would be interesting when similar observations could be made at a temperature nearer T'_k.

[1] WIEDEMANN's Annalen. XVII p. 390. 1882.

Physics. — *"On the use of the audion in wireless telegraphy"*. By D. Coster. (Communicated by Prof. H. A. Lorentz).

In the recent successes in wireless telegraphy the three-electrode-relais or audion has played the most important part. The audion consists of a vacuum tube, in which are fused three electrodes: a hot wire-kathode k, a usually flat anode a and a third auxiliary electrode h, placed between the other two and consisting of a few parallel and mutually connected metal wires, which is therefore called the grid. The properties of the audion are determined by the audion-characteristics, which give the relation of the currents i_a and i_h on the one side and the potentials e and r on the other. (See fig. 1). The current i_h is usually very small compared to i_a and it may be neglected in many cases. A simple scheme for the determination of the characteristics is given by fig. 1, where for the sake of simplicity the measuring instruments are not indicated. Fig. 2 gives i_a as a function of e, for different values of r. The different characteristics may be deduced from one another by parallel translation. Fig. 3 gives i_a as a function of v, while e is a constant.
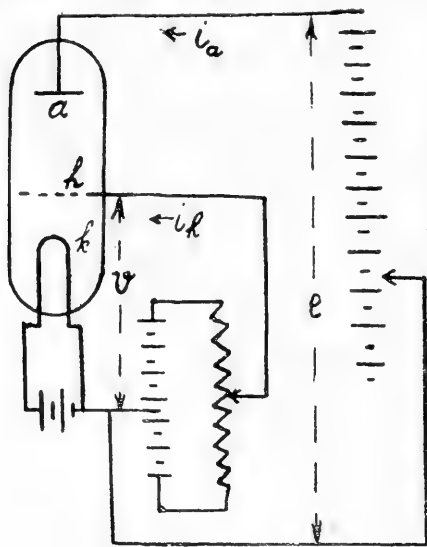
Fig. 1.
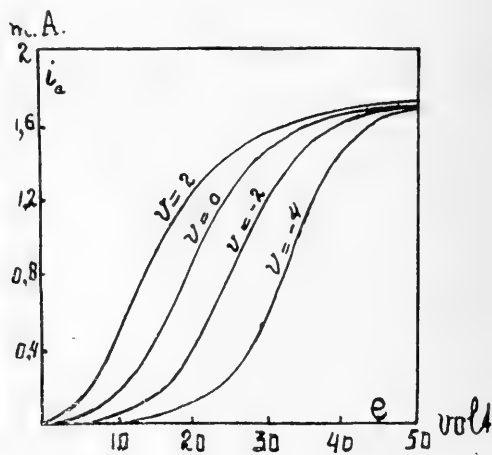
Fig. 2.

These characteristics are similar to those of fig. 2; as a rule however they are steeper. Figs. 2 and 3 give the essential features of the audion-characteristics; the different forms of audions show more or less important deviations.
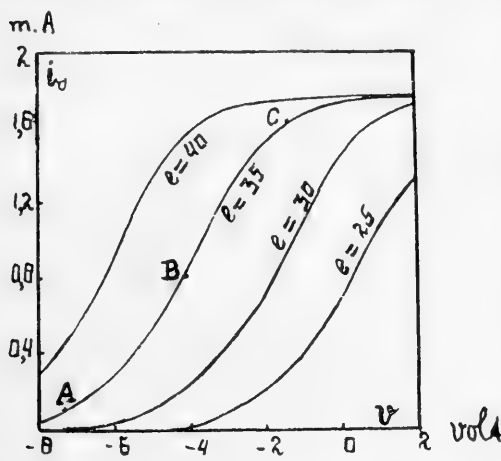
Fig. 3.

Though the character of the gas and the degree of its rarefaction are very important in the determination of the individual properties of the audion, they are problably not of essential signification. At any rate LANGMUIR [1]) has succeeded in constructing a normally functioning three-electrode-relais, which he calls pliotron, from which every trace of gas seems to have been removed. In the following discussion we may therefore assume that the electric conduction in the audion is exclusively performed by the thermoions.

For the number N of electrons, which in the unit of time enter the vacuum from the hot wire, RICHARDSON found the well-known formula:

$$N = a T^\lambda e^{-\frac{b}{T}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

here T is the absolute temperature of the hot wire, a and b are constants, λ is a quantity which differs but little from unity. The emerging electrons may be caught on an anode opposite the kathode; N is then determined by a current-measurement. When T is constant, the current increases at first with increasing potential-difference. It is only the maximum current, "the saturation current", which in its dependence on the temperature follows RICHARDSON's formula.

To explain this initial increase of the current with the impressed voltage LANGMUIR [2]) gave his theory of the space-charge. The electrons in the field between the kathode and the anode diminish the potential-gradient in the neighbourhood of the kathode. When this

[1]) LANGMUIR: General Electr. Rev. (1915) p. 327.
    See also HUND: Jahrb. f. Drahtl. Tel. (1916) 10 p. 521.
[2]) Phys. Rev. (1913) p. 457.

gradient is zero part of the emerged electrons may fall back on the kathode. This theory led LANGMUIR to the formula [1]):

$$i = CV^{\frac{3}{2}} \qquad \ldots \qquad \ldots \qquad \ldots \qquad (2)$$

Here i is the current as long as it remains below the saturation current, V is the impressed voltage, C is a constant which depends on the form and the distance of the electrodes. In the neighbourhood of saturation, i approaches a constant value.

This relation between the thermoionic current and the impressed voltage will be found in the characteristics of fig. 2 and 3. A complication is here caused by the presence of the third electrode, the grid, about which we may make the following observations. As a rule the audion is used with tensions of such values that we should have a saturation-current, if no grid were used. It is the function of the grid to retard more or less the electrons emitted by the kathode. The potential of the grid is therefore always chosen lower than the potential which we should have at that place, if the grid were removed. Usually the grid-potential is not much different from the average kathode-potential, in many cases it is even a little lower. Of the electrons, which reach the plane which we can draw through the grid, by far the greater part will escape between the grid-wires to the anode and but few will strike the grid. The usually small surface of the wires also contributes to this effect. Thus the grid current i_k (see fig. 1) is in normal working conditions small as compared to the anode-current i_a. The latter not only depends on the anode-potential e, but also on the grid-potential v. We cannot go far wrong in taking as "driving force" of i_a the mean potential in the plane of the grid. Denoting by φ this mean potential, φ is, as long as the anode-current has not yet reached its maximum, a linear function of e and v

$$\varphi = \alpha e + \beta v \qquad \ldots \qquad \ldots \qquad \ldots \qquad (3)$$

At first therefore we get for the anode-current the following relation:

$$i_a = C (\alpha e + \beta v)^{\frac{3}{2}} \qquad \ldots \qquad \ldots \qquad \ldots \qquad (4)$$

An analogous empirical formula is given by LANGMUIR [1]) for his pliotron.

In wireless telegraphy the audion is used as rectifier and as

[1]) An analogous formula had been given before by CHILD for the transport of pos. ions. See Phys. Rev. (1911) p. 492.

[1]) See HUND: Jahrbuch f. Dr. Tel. (1916) 10 p. 521.

amplifier. Following the characteristics of fig. 3 we can easily check these functions. When the instantaneous condition of the audion is given by the point B on one of the characteristics, we see that small fluctuations of the grid-potential involve relatively large alterations of the anode-current. Owing to the linearity of the characteristics in the neighbourhood of B, these current-fluctuations are proportional to the variations of the grid-potential. Here it is of great importance, that the grid itself receives but little current "it reacts upon tensions"; very small energies are therefore sufficient to cause the alterations of the grid-potential. At the points A and C the audion acts at the same time as rectifier: to equal potential-variations in positive and negative sense correspond different current-variations.

Of late years it has been found that the audion can perform yet a third function. By a suitable arrangement we can form an unstable system, which gives rise to alternating currents of definite frequency, as in the so-called musical arc. Furthermore it has been found that the unstable connections increase to a high degree the amplifying action, so-called "back-coupling". For a good insight into the use of the audion in wireless telegraphy it is of importance to understand its generative action.
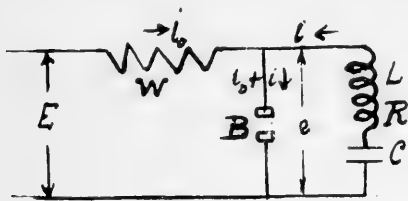
Fig. 4.

The question of the instability of electrodynamical systems mechanically at rest has been studied among others by SIMON and his pupils [1]). These investigators have succeeded in establishing some general rules which are easily obtained by the aid of a simple diagram (see fig. 4).

E is a constant electromotive force, W is a resistance which is so large, that compared with it the variable resistance of the arc B is negligible, L is a selfinduction, whose resistance is R, C is a capacity. Owing to the assumption with regard to W, the current i_0 may be considered as a constant. We assume that the arc-tension is only a function of the arc-current $i_0 + i$, which is linear for small values of i. For this problem we therefore arrive at linear differential equations, whose general solution consists in a "continuous-current-solution" and an "alternating-current-solution", which may be considered independently of each other. Thus the tension e may

[1]) Phys. Zeitschr. (1902) III p. 282.
    „   „   (1903) IV p. 366 and p. 737.
    See also Jahrb. f. Dr. Tel. (1918) 1 p. 16.

be represented by a constant tension e_0 augmented by an alternating tension e_1; for the current the division into i_0 and i has already been made.

For the oscillation-circuit, consisting of arc, selfinduction and capacity we have:

$$e + Ri_1 + L \frac{di_1}{dt} + \int \frac{i_1 dt}{C} = 0, \quad \cdots \quad \cdots \quad (5)$$

giving by differentiation:

$$L \frac{d^2 i_1}{dt^2} + \left(R + \frac{\partial e}{\partial i_1} \right) \frac{di_1}{dt} + \frac{i_1}{C} = 0 \quad \cdots \quad \cdots \quad (6)$$

Hence it follows that continual alternating currents can only exist, if:

$$\frac{\partial e}{\partial i_1} = - R \quad \cdots \quad \cdots \quad \cdots \quad (7)$$

It is thus necessary that an increase in the current involves a decrease of tension and inversely, in other words: the condition for the generation of alternating currents is a falling arc-characteristic. For the alternating current the arc behaves as a "negative resistance" hence the quantity $-e$ may be considered as the electromotive force for the alternating current.

Applying this to the audion, we see from the characteristics of fig. 2, that for a *constant* gridpotential, it has a *rising* characteristic, hence it is *stable*. Only by coupling the grid to the oscillation-circuit it is possible to make the system *unstable*.

The anode current i [1]) is a function of the anode-potential e and the grid-potential v;

$$i = f(e,v) \quad \cdots \quad \cdots \quad \cdots \quad (8)$$

If here also we assume a linear relation between current and tensions, the general solution of the differential equations for this system consists of the sum of a "continuous-current-solution" i_0, e_0, v_0 and an "alternating-current-solution" i_1, e_1, v_1. Here again the quantity $-e_1$ is to be considered as the electromotive force for the alternating current.

From (8) it follows that

$$i_1 = \frac{\partial f}{\partial e} e_1 + \frac{\partial f}{\partial v} v_1 \quad \cdots \quad \cdots \quad \cdots \quad (9)$$

Putting $\dfrac{\partial f}{\partial e} = \dfrac{1}{r}$ and $\dfrac{\dfrac{\partial f}{\partial v}}{\dfrac{\partial f}{\partial i}} = \lambda$, this becomes:

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[1]) For the sake of convenience we henceforth leave out the index a.

$$- e_1 = \lambda\, v_1 - r\, i_1. \quad \cdots \quad \cdots \quad (10)$$

From (10) we see in connection with the above discussion that, if we are at the proper point of the characteristic (e.g. B in fig. 3) and the grid is subjected to potential-fluctuations v_1, we may consider the audion as an alternating current-generator with an electromotive force λv_1 and an internal resistance r. The potential-fluctuations of the grid may be caused by an external electromotive force. But they may also be produced by coupling the grid in a proper manner to the anode-circuit, by which an oscillation when once arising, maintains itself. Both methods find manifold application in wireless telegraphy. The second method will be especially discussed here. In doing so we shall make use of the method of "complex resistances", which is customary in alternating-current-theory; the following remarks on this method may be useful.

We suppose an arbitrary electric system, consisting of self-inductions, capacities and resistances, in which somewhere an electromotive force $E \cos pt$ is applied. The currents which arise in the system, satisfy a set of linear differential equations [1]) of the form:

$$\Sigma\, R_h\, i_h + L_h \frac{di_h}{dt} + \int \frac{i_h\, dt}{C_h} = \begin{cases} 0 \\ E \cos pt \end{cases} \quad \cdots \quad (11)$$

where the summation is to be extended over all the currents occurring in any closed circuit which can be described in the system. The solution of (11) consists of the general solution of a set of homogeneous linear equations, which are obtained from (11) by putting $E \cos pt = 0$, and a particular solution. The first part of the solution gives the (damped) free vibrations of the system; the second part the forced vibration. To discover the particular solution use can be made of the complex notation by putting $E\, e^{jpt}$ for $E \cos pt$, where $j = \sqrt{-1}$; and by trying for i_h a solution of the form $A_h\, e^{jpt}$; A_h is complex and gives not only the amplitude but also the phase-shift of i_h.

Instead of (11) we thus obtain a set of linear algebraic equations of the form:

$$\Sigma \left\{ R_h + j\left(p\, L_h - \frac{1}{pC_h} \right) \right\} A_h = \begin{cases} 0 \\ E \end{cases} \quad \cdots \quad (12)$$

Equations (12) are analogous to KIRCHHOFF's equations for a direct-current-system, only in the present case complex resistances occur of the form $Z_h = R_h + j\left(pL_h - \frac{1}{pC_h} \right)$. Therefore the same rules may

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[1]) At the same time they satisfy algebraic equations of the form $\Sigma i_k = 0$:

be applied as in direct-current-problems. For instance two parallel resistances z_1 and z_2 may be replaced by one single resistance $\dfrac{Z_1 Z_2}{Z_1 + Z_2}$.
If there are also mutual inductions M_r in the system, the left-hand part of (12) is to be completed by terms of the form $jp_r M_r A_r$. In that case the method of complex resistances is still applicable though the analogy with direct-current-problems now does not hold entirely.

We shall now apply the method to the audion. By a system of self-inductions, capacities and resistances the anode is connected with the kathode; the grid is coupled with this circuit either by a direct contact, or by means of one or more mutual inductions. Further there are two batteries in the system, which provide for the mean tensions e and v being such that we are operating at the proper point of the characteristics (e.g. B in fig. 3). For alternating currents the batteries behave as ordinary resistances. Since we are only concerned with the alternating currents and tensions we shall henceforth for the sake of convenience omit the indices to these quantities. (See e.g. (10)).

Hence we obtain for the audion a same set of equations as (11), $E \cos pt$ now having the value λv, where v is the alternating part of the grid-potential. These can again be reduced to a set of equations (12). The grid-potential, however, in its turn is a function of the currents in the anode-circuit. Hence (12) is to be completed by one equation of the form:

$$E = \lambda \, \Sigma \, B_r A_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where the B_r's in general are complex quantities.

If for a given connection we can find a set of A's which satisfy (12) and (13) for a real value of p, this connection has a generative action. Many of such connections have been published in almost confusing abundance. A summary is for instance given by Armstrong [1]) and by Eccles [2]).

From the above we may deduce the following general rules for the generative audion-connections:

A. If a connection is found, which gives alternating currents of a definite frequency, we can deduce from it others, which give currents of the same frequency by replacing the "alternating resistances" by others which are equivalent for this frequency. In this

[1]) See Jahrb. f. Dr. Tel. (1918) 12, p. 241.
[2]) Electrician July 1916, p. 573, Aug. 1916, p. 595.
See also: Yearbook of Wireless Tel. (1917) p. 674.

manner two parallel alternating resistances Z_1 and Z_2 may be replaced by a single one of the value $\dfrac{Z_1 Z_2}{Z_1 + Z_2}$.

B. We can also find other connections by replacing all the alternating resistances by their conjugate complex values. Indeed in this case there is a set of A's conjugate complex to the former A's which also satisfy (12) and (13) for a real value of p. In the case that there are no mutual inductions in the circuit, this can be obtained by replacing every self-induction L_h by a capacity C'_h and inversely, such that $L_h\, C'_h = L'_h\, C_h = p^2$. If mutual inductions also occur this simple substitution is no longer applicable [1]). Besides in this case the mutual induction must change its sign. This may be arrived at by changing the terminals on the primary or the secondary side.

On the ground of the above general rules we may draw the following conclusions with regard to the generative connections:

There are two types of connections:

I. Those with direct coupling. Here the grid is immediately connected to a point of the oscillation-circuit.

II. Those with *indirect* coupling. Here the grid is coupled by means of one or more mutual inductions with the anode-circuit.

I. *Direct coupling.*

The general type of these connections, to which they can all be reduced according to rule A, is given by fig. 5. $z_1 = z'_1 + z''$ and z_2 [2]) are alternating-current-resistances; r and λ have the same signification as in (10).
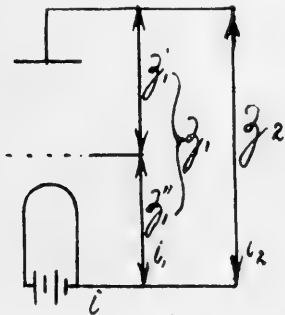
Fig. 5.

The relations (12) and (13) change into:

$$\left(r + \frac{z_1 z_2}{z_1 + z_2}\right) i = \lambda v \quad . \quad . \quad (14)$$

$$v = -z''_1 i_1 = -\frac{z''_1 z_2}{z_1 + z_2} i \quad : \quad . \quad . \quad . \quad : \quad (15)$$

By combination of (14) and (15) we get:

$$r + \frac{z_1 z_2}{z_1 + z_2} + \lambda \frac{z''_1 z_2}{z_1 + z_2} = 0 . \quad . \quad . \quad . \quad (16)$$

[1]) (Note to the English translation). Prof. ELIAS has kindly pointed out to me, that in this case a wholly symmetrical substitution is obtained by changing the mutual induction into a "mutual capacity" (two condensers telescoped into each other).

[2]) In the fig. denoted by gothic letters.

By substituting $z_1 = x_1 + jy_1$ etc., where $j = \sqrt{-1}$ and putting the real and the imaginary parts of (16) separately equal to zero, we obtain:

$$x_2 \{ x_1' + (1 + \lambda) x_1'' \} + r (x_1 + x_2) - y_2 \{ y_1' + (1 + \lambda) y_1'' \} = 0 \quad (17)$$

$$y_2 \{ x_1' + (1 + \lambda) x_1'' \} + r (y_1 + y_2) + x_2 \{ y_1' + (1 + \lambda) y_1'' \} = 0 \quad (18)$$

The y's and possibly also the x's contain the frequency p. By eliminating p from (17) and (18), we obtain a relation for the constants of the circuit:

$$\psi (r, R_1 L_1 C_1 \ldots) = 0 \ . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

which must be satisfied, in order that permanent alternating currents may exist. Besides either of the equations (17) and (18) can be employed for the determination of the frequency. (19) gives a *necessary* condition; it is also *sufficient*, if (17) or (18) contains one real root.

If p has a real value, x_1, x_2 etc. are essentially positive as having the character of ohmic resistances; r and λ are positive audion-constants; $y_1, y_2 \ldots$ are either positive (of the nature of a self-induction) or negative (capacity). From (17) and (18) it is obvious, that connection I can only be made in two essentially different manners. From (17) it may be concluded, that y_2 and $y_1' + (1 + \lambda) y_1''$ must have the same sign, from (18) it follows, that $y_1 = y_1' + y_1''$ and y_2 must be of a different sign.

First manner:

y_2 and y_1'' positive; y_1' negative, whereas

$$y_1'' + y_2 < - y_1' < (1 + \lambda) y_1'' \ . \quad . \quad . \quad . \quad . \quad (20)$$

This connection in its simplest form is given by fig. 6. Now (20) assumes the form:

$$p (L_1 + L_2) < \frac{1}{pC_1} < (1 + \lambda) pL_1$$

hence it follows that

$$L_2 < \lambda L_1.$$

Instead of (17) and (18) we obtain:

$$R_1 R_2 (1 + \lambda) + (R_1 + R_2) r + \frac{L_2}{C_1} - (1 + \lambda) p^2 L_1 L_2 = 0$$

$$p L_2 R_1 (1 + \lambda) + r \left\{ p (L_1 + L_2) - \frac{1}{pC_1} \right\} + R_2 \left\{ - \frac{1}{pC_1} + (1 + \lambda) pL_1 \right\} = 0$$

whence by elimination of p the rather complicated condition for oscillation can be deduced.
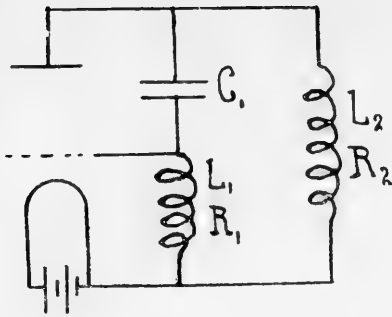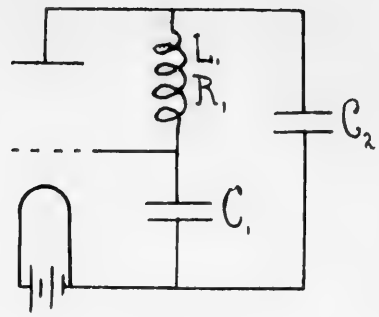
Fig. 6.   Fig. 7.

Second manner.

This can be obtained from the former by the substitution B, y_2 and y''_1 are here negative and y'_1 positive, whereas

$$- (y_1'' + y_2) < y_1' < - (1 + \lambda)\, y_1''$$

Fig. 7 gives the simplest form. The relations (17) and (18) here give respectively:

$$p^2 = \frac{1 + \lambda}{L_1\, C_1 + r\, R_1\, C_1\, C_2} \quad \cdots \quad \cdots \quad (21)$$

$$p^2 = \frac{1}{L}\left(\frac{1}{C_1} + \frac{1}{C_2} + \frac{R}{rC_2} \right) \quad \cdots \quad \cdots \quad (22)$$

Connections, which belong to the type of fig. 7, are frequently applied. They have been dealt with theoretically by Vallauri [1]). Connections of the type of fig. 6 also occasionally find an application [2]).

II. *Indirect coupling.*

The simplest case to deal with is that, where the grid-circuit is currentless. The reduced type of this connection is given by fig. 8. Here
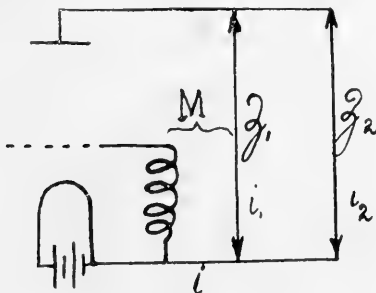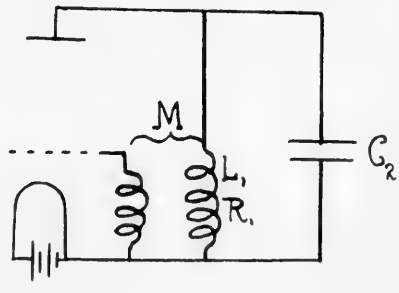
Fig. 8.   Fig. 9.

[1]) See Jahrb. f. Dr. Tel. (1918) 12 p. 381.

[2]) See e.g. Armstrong l.c., fig. 13. The capacity, which we have called C_1 in fig. 6, is absent here. The anode and the grid, however, which are sealed in at the same end of the audion, have sufficient capacity with respect to each other.

$$\lambda v = \left(r + \frac{z_1 z_2}{z_1 + z_2} \right) i \quad \cdots \quad \cdots \quad (23)$$

$$v = -jp M i_1 = -jp M \frac{z_2}{z_1 + z_2} i \quad \cdots \quad (24)$$

From (23) and (24) it follows that

$$\lambda p M y_2 = r (x_1 + x_2) + x_1 x_2 - y_1 y_2 \quad \cdots \quad (25)$$

$$- \lambda p M x_2 = r (y_1 + y_2) + x_1 y_2 + x_2 y_1 \quad \cdots \quad (26)$$

These equations can only be satisfied in two manners, which by substitution B can be deduced from each other:

First manner: y_1 pos., y_2 neg., M neg.

Second manner: y_1 neg., y_2 pos., M pos.

They are given by fig. 9 and 10.
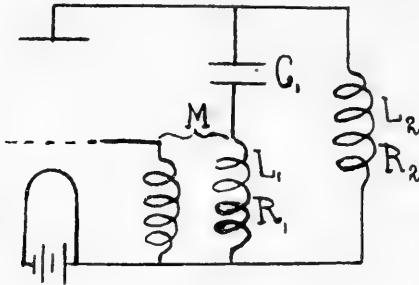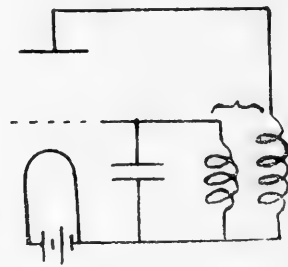
Fig. 10.   Fig. 11.

The connection of fig. 9 is also frequently made use of. It was thoroughly discussed by VALLAURI[1]). That of fig. 10 so far has apparently not been used.

If the indirect coupling is applied and there is also a current in the grid-circuit, the arbitrariness is so great, that it seems rather difficult to establish any general rules, except the substitution-rules A and B. Still for every special case the above calculation leads directly to the result and gives a better survey than the solution of a set of simultaneous differential equations. A simple instance of these connections is given by fig. 11; they occur very often.

The same connections, which will make the audion generate, are also exceedingly suitable for giving a good amplifying action. Whether an audion acts as a generator, depends in the end on the roots of an algebraic equation of the nth degree:

$$a_0 p^n + a_1 p^{n-1} \cdots + a_n = 0. \quad \cdots \quad \cdots \quad (27)$$

This equation has been obtained from a homogeneous linear differential equation of the nth order:

$$a_0 \frac{d^n x}{dt^n} + a_1 \frac{d^{n-1} x}{dt^{n-1}} + \cdots + a_n = 0, \quad \cdots \quad \cdots \quad (28)$$

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[1]) See l.c.

by trying a solution of the form $x = Ae^{pt}$. Here the a's are functions of the alternating current-resistances; x indicates a current or a tension.

If at least one root $p = p_0$ is a pure imaginary quantity, free un-damped vibrations can occur. Where the audion is applied in a receiving station for wireless telegraphy, the grid-potential is subjected to a forced vibration on account of the coupling with the antenna. Instead of (28) we now obtain an equation with a right-hand side of the following form, in complex notation [1]):

$$a_0' \frac{d^n x}{dt^n} + a_1' \frac{d^{n-1} x}{dt^{n-1}} \dots + a_n' = E e^{p't} \quad . \quad . \quad . \quad (29)$$

where p' is a pure imaginary quantity.

The particular solution, which gives the forced vibration is found by putting $x = A'e^{p't}$. To determine the amplitude A', we have:

$$|A'| = \frac{E}{|a_0' p_n' + \dots a_n'|} \quad . \quad . \quad . \quad . \quad (30)$$

If p' is equal to an (imaginary) root p_0 of (27), we can make the denominator of the right-hand side of (31) as small as we like, by making the constant a' but little different from a_0 etc. in (27). A limit is only given by the condition, that the natural vibrations determined by:

$$a_0' p'^n + \dots a_n' = 0 \quad . \quad . \quad . \quad . \quad . \quad (31)$$

have to be sufficiently damped; therefore it is necessary that the roots of (32) have a sufficiently large real part. Hence by a coupling as that of fig. 12 the object is attained of the system having but little friction for the forced vibration.
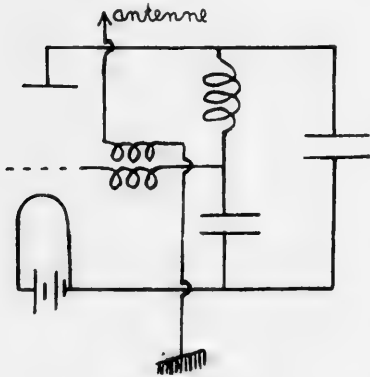
Fig. 12.

The audion is exceedingly well adapted to receive undamped waves. According to the heterodyne-principle local oscillations are then excited in the receiving station, which give rise to beats of audible frequency which can be detected in the ordinary manner by rectifier and telephone. The audion is then tuned in such a way, that the natural frequency differs but slightly from that of the forced vibration. It is then obvious that the system for this vibration has but little "friction".

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[1]) We reserve the a's without accents for the special case, that these quantities are chosen in such a manner that (27) has one root, which is a pure imaginary quantity.

In the foregoing considerations we have assumed that a linear relation holds between current and tension. From the fig. 2 and 3, however, it appears that this it only true for a limited part of the characteristics. The current-amplitude cannot rise above a definite value. It follows that actually we have not to ask for the pure imaginary roots of (27), but for the roots with a positive real part. By an investigation as given above we only get to know the points, where the real part of the roots p changes its sign. It appears to me that in most cases this will be sufficient to discover the different coupling-possibilities.

In an American patent of Nov. 1917 (N°. 102, 503) the use of the audion as generator is described, where especially the *quadratic* terms in the current-tension relation seem to assume the most important part. It is rather difficult to draw conclusions from patent-descriptions and as far as I know a discussion of such a coupling has thus far not been published.

Chemistry. — *"Urease and the radiation-theory of enzyme action"*, II. By Dr. H. P. BARENDRECHT. (Communicated by Prof. J. BÖESEKEN.)

In order to secure a more complete constancy of p_H a more extensive investigation, this time with 0,01 °/$_0$ of urea, was carried out some months later, when the technique of the estimations was more fully worked out and refined.

At least two series, with different p_H, were completed on the same day, starting from the same neutral phosphate extract of Soja-meal. On another day one of them was repeated together with a third one with a new p_H. In this way the uncertainty as to the comparability of the enzyme quantities, prepared on different days, was obviated.

For want of space these tables cannot be communicated here. The value of m, now calculated with the formula $\dfrac{nc}{0,434} \log \dfrac{1}{1-y} +$ $0,01y = mt$, was constant in each table again, within the limits of the unavoidable experimental errors.

In continuing these investigations at still higher p_H a falling off of the constant m was generally observed towards the end of the reaction. This is, what might have been expected for different reasons.

From the well-known chart of the H-ion concentration data of SÖRENSEN it is clear, that the phosphate mixtures are only efficient buffers up to about $p_H = 8$.

It was for instance established by the present author, that, while 10 c.c. of a 9,6 °/$_0$ phosphate mixture, diluted with 2 c.c. of water, produced an 8 °/$_0$ phosphate mixture of $p_H = 8,11$, dilution with 2 c.c. of NH$_3$ $\frac{1}{50}$ N (i.e. the amount of NH$_3$ formed by the hydrolysis of 12 c.c. of 0,01 °/$_0$ urea solution) made $p_H = 8,25$.

At lower p_H this change in p_H is only about 0,01 or 0,02.

Evidently by the increase of alkalinity during the hydrolysis in a solution of 0,01 °/$_0$ urea the m already diminishes a little in the case of a large p_H.

Moreover, as indicated above, the radiation theory itself predicts a decrease of the activity of the enzyme as soon as the total concentration of urea + H-ion (or more accurately, as soon as $m + nc$) has become so small, that the radiation does not all reach a urea

molecule or an H-ion before it has lost its power by spreading. In
the very dilute solutions of 0,01 °/₀ urea and of low H-ion concen-
tration this effect may certainly be expected, especially if a great
deal of the urea has been hydrolysed.

As will be explained further on, a decrease of m in these alkaline
solutions may also be brought about in the course of time by the
reversed action, the synthesis of urea.

TABLE 12.

	Concentration of urease.	p_H	m, for unit of urease concentration.
May 24th, 1918	3	5.84	0.000205
May 24th, 1918	3	6.13	0.000221
May 24th, 1918	3	6.40	0.000267
March 2nd, 1917	3	6.40	0.00027
March 1st, 1917	3	6.40	0.000263
March 1st, 1917	3	6.67	0.000347
Febr. 26th, 1917	2	6.67	0.00036
Febr. 26th, 1917	2	7.0	0.000525
March 6th, 1917	1	7.0	0.00050
March 6th, 1917	1	7.21	0.00067
Jan. 22nd, 1917	$\frac{1}{2}$	7.21	0.00067
Jan. 22nd, 1917	$\frac{1}{2}$	7.52	0.000752
Jan. 22nd, 1917	$\frac{1}{2}$	7.64	0.000689
March 12th, 1917	$\frac{3}{8}$	7.64	0.000717
March 12th, 1917	$\frac{1}{4}$	7.80	0.00060
March 9th, 1917	$\frac{1}{2}$	7.80	0.000646
March 9th, 1917	$\frac{3}{10}$	8.03	0.000467
March 23rd, 1917	$\frac{6}{10}$	8.03	0.000479
March 23rd, 1917	$\frac{6}{13}$	8.13	0.000405
April 3rd, 1917	$\frac{6}{13}$	8.13	0.000431
April 3rd, 1917	$\frac{6}{13}$	8.65	0.000245
March 22nd, 1917	$\frac{3}{10}$	8.03	0.000453
March 22nd, 1917	$\frac{3}{13}$	8.13	0.000388
April 5th, 1917	$\frac{3}{13}$	8.13	0.000416
April 5th, 1917	$\frac{3}{13}$	8.65	0.000423

In the experimental verification of the formula $\dfrac{nc}{0{,}434} \, log \, \dfrac{1}{1-y} \; +$
$ay = mt$ there is, however, besides a lowering of the H-ion concentration, another way to change the relation between the coefficients of $log \, \dfrac{1}{1-y}$ and of y.

If only p_H can be kept constant, we may raise a, the concentration of the urea, considerably. The realisation of this method will be communicated further on in this paper.

For the above mentioned reasons at high p_H only the first values of m have been used for the main present purpose: the determination of m at different H-ion concentration.

For the purpose of comparing the values of m obtained, they are all reduced to the same enzyme concentration, the unit of which is again arbitrarily chosen as resulting when 1 g. of Soja is extracted in 100 c.c. of water $+\, 7.28$ g. of Na_2HPO_4 2 aq $+\, 2{,}32$ g. of KH_2PO_4 and 50 c.c. of filtrate of this is mixed with 100 c.c. of water $+\, 9{,}6$ g. of phosphate.

m as a function of p_H.

According to the mathematical formulation of the radiation theory, $-dx = m \, \dfrac{x}{x+nc} \, dt$, the constant m is only dependent on the concentration of urease present.

When equal concentrations of urease are compared or the effect has been reduced to equal concentrations, i. e. when the enzyme concentration is kept constant as well as the temperature, m will be proportional to the activity of the same urease concentration.

From table 12 it is clear, that the activity m changes with p_H in a peculiar manner.

In figure 3 the mean values of m, in arbitrary units, are plotted against the values of p_H as abscissae. The strikingly regular curve, thus obtained, allows a further mathematical treatment to elucidate the nature of urease.

MICHAELIS [1] had already shown, that enzyme activity, represented as a function of p_H gives in many cases a curve somewhat similar to that of the undissociated part of an amphoteric electrolyte. The vagueness and irregularity of the curves of MICHAELIS and of those of SÖRENSEN for invertase excluded, however, all further comparison and analysis.

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[1] Die Wasserstoffionen-Konzentration. Verlag von JULIUS SPRINGER, 1914.

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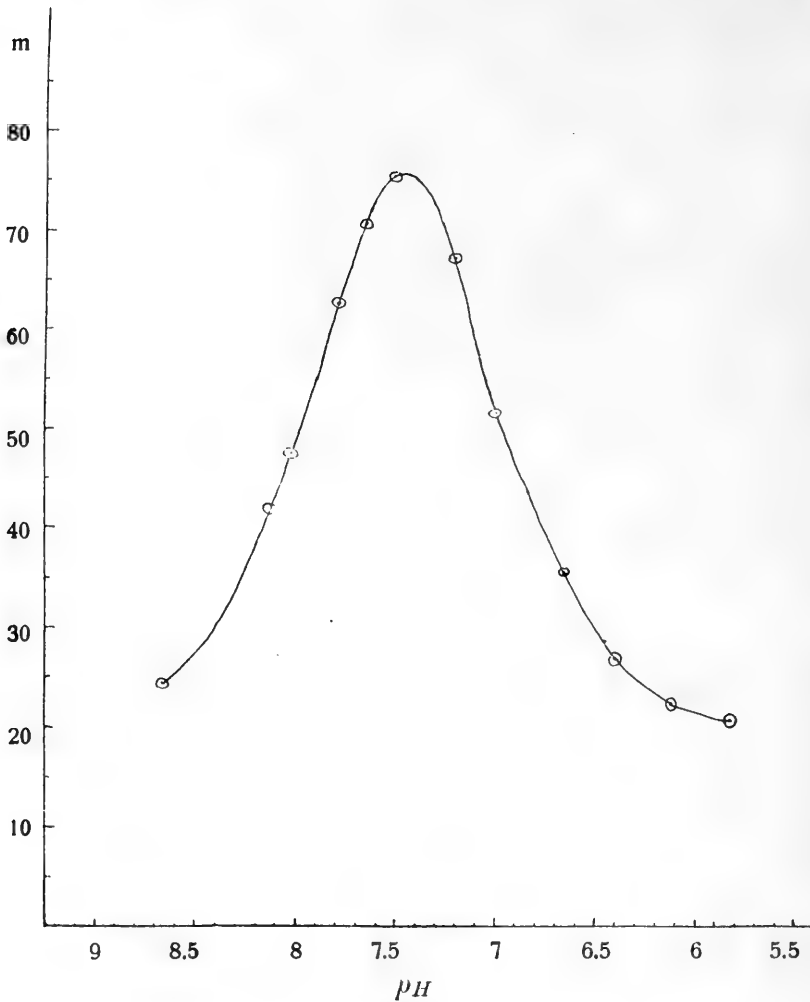
p_H
Fig. 3.

It is to be remembered, that the activity m, as calculated according to the radiation theory, is quite different from what had hitherto been empirically determined as activity.

. This is immediately clear from the formula

$$m = \frac{\dfrac{nc}{0,434} \, log \, \dfrac{1}{1-y} + ay}{t}$$

The observed effect y in a given time t is evidently by no means proportional to m.

The above mentioned regularity in m and the results, connected with it, which will be recorded further on, therefore adduce considerable experimental evidence for the radiation theory.

In the work of MICHAELIS attention is drawn to the fact, that a representation of the undissociated part of an amphoteric electrolyte as a function of the H-ion concentration, taking as abscissae the values of p_H, instead of those of the H-ion concentration itself, presents the advantage of producing curves of far more characteristic type.

His "rest-curves" are derived as follows:

Calling (A) the total concentration of the amphoteric electrolyte, $(A+)$ that of the kation, $(A-)$ that of the anion, the concentration of the undissociated rest (x) is:

$$(x) = (A) - (A+) - (A-).$$

According to the law of mass action we have in the solution the two equations of equilibrium:

$$(A+)(OH) = k_b(x)$$
$$(A-)(H) = k_a(x).$$

Therefore

$$(x) = (A) - (x)\frac{k_b}{(OH)} - (x)\frac{k_a}{(H)},$$

from which

$$(x) = \frac{(A)}{1 + \frac{k_a}{(H)} + \frac{k_b}{(OH)}}$$

The undissociated fraction $\varrho = \frac{(x)}{(A)}$ becomes

$$\varrho = \frac{1}{1 + \frac{k_a}{(H)} + \frac{k_b}{(OH)}}.$$

For the sake of comparison the curves, drawn by MICHAELIS for different values of the dissociation-constants k_a and k_b, are reproduced in Figure 4.

The resemblance of our diagram of urease activity m to these curves is obvious.

It is to be borne in mind, however, that the relative dimensions of p_H and ϱ are, of course, arbitrary in these figures.

Evidently, at least with decreasing p_H, where the experiments could be pushed farther than on the other side, m tends not to zero, but to a value of about 18.

The interpretation of these results is therefore as follows:

Urease is an amphoteric electrolyte, whose activity is greatest when undissociated. When the asymptote, to which m approaches,

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is drawn as a new axis of abscissae, the curve represents the excess of activity of undissociated over dissociated urease.
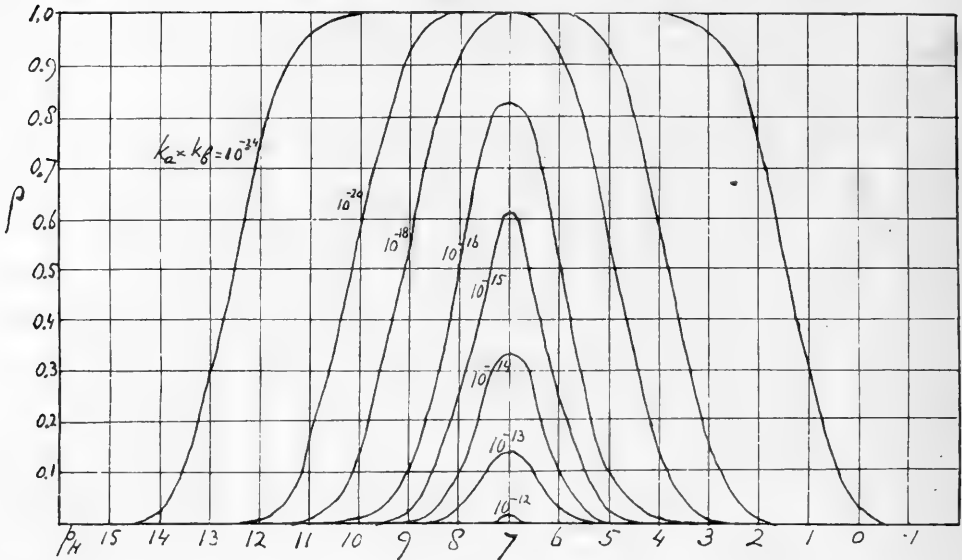
Fig. 4.

Thus

$$m - \beta = \frac{\alpha}{1 + \dfrac{k_a}{(H)} + \dfrac{k_b}{(OH)}}$$

The constant α, expressing the proportionality between the activity as determined (in arbitrary units) and the undissociated fraction, had to be calculated from the experiments as well as the constants k_a and k_b.

The term β, which appears to be about 18 from a provisional survey of the curve, had, in point of fact, also to be determined more accurately in the same way.

These calculations required the knowledge of the hydroxyl-ion concentration (OH) as well as of the hydrogen-ion concentration (H).

In water or dilute solutions this value is immediately given by the dissociation-equation of water:

$$(H)(OH) = k_w$$

Since an 8°/₀ phosphate solution, however, is not to be regarded as a dilute solution, special determinations of the hydroxyl-ion concentration were indispensable.

The experiments, by which these were carried out, are described in the last part of this paper.

The simplest method of calculation appeared to be giving provi-

sionally a definite value to β, for instance 18. By then combining the equations, say for $p_H = 7.52$ and for $p_H = 7$, α was eliminated directly. The same process, applied to the equations for $p_H = 6.40$ and for $p_H = 8.03$, afforded a second equation, in which only k_a and k_b were unknown. From these two equations k_a and k_b were calculated.

In table 13 are summarised the values found for p_H and p_{OH}, the concentration of the H-ions and OH-ions (multiplied by 10^8) determined and those calculated on the basis of three different values of β.

TABLE 13.

p_H	p_{OH}	$10^8 (H)$	$18^8 (OH)$	$10^5\ m$ determined	$10^5\ m$ calculated for:		
					$\beta = 18$	$\beta = 17.9$	$\beta = 19$
5.84	7.94	144.5	1.15	20.5	20.6	20.5	21.6
6.13	7.65	74.13	2.24	22.1	23.—	22.9	24.—
6.40	7.38	39.81	4.17	26.7	27.2	27.1	28.2
6.67	7.11	21.38	7.76	35.4	35.—	34.7	35.7
7.0	6.78	10.—	16.6	51.3	51.3	51.3	51.3
7.21	6.57	6.17	26.92	67.—	64.8	64.9	64.—
7.52	6.26	3.02	54.95	75.2	75.2	75.2	75.2
7.64	6.14	2.29	72.44	70.3	72.4	72.2	73.7
7.80	5.98	1.59	104.7	62.3	64.—	63.6	66.9
8.03	5.75	0.93	177.8	47.3	49.—	48.7	53.—
8.13	5.65	0.74	223.9	41.7	43.4	43.1	47.3
8.65	5.13	0.22	724.4	24.4	26.—	25.9	28.—

Taking β to be 18 or 17.9, the differences of m determined and m calculated are not larger than, according to table 12, the different values of m at the same p_H determined on different days; hence not larger than the uncertainty, left in their experimental estimation.

For $\beta = 19$ the deviations are distinctly larger.

For $\beta = 17.8$ the calculation from the above four values of m produced a negative k_a. Hence the minimum value of β would be about 17.9.

The results of these calculations, as regards k_a, k_b and α are summarised as follows:

TABLE 14.

β	k_a	k_b	x
17.9	$10^{-8} \times 1293$	$10^{-8} \times 20880$	46356
18.—	$10^{-8} \times 132.6$	$10^{-8} \times 2170$	4828
19.—	$10^{-8} \times 10.8$	$10^{-8} \times 206.5$	469.3

It is to be borne in mind, that the equation

$$m - \beta = \cfrac{a}{1 + \cfrac{k_a}{10^{-pH}} + \cfrac{k_b}{10^{-pOH}}},$$

from which these constants had to be calculated, is an exponential one. Slight variations in pH must therefore be expected to have a large influence.

However, as the deviations between the experimental curve and that, representing the calculated values of m for, say $\beta = 18$, in table 13, are within the limits of accuracy, set by the experimental methods employed, it may be concluded, that the equation for the undissociated part of an amphoteric electrolyte represents fairly well the activity of urease as a function of pH.

An important consequence of this is the possibility of obtaining at least an approximate knowledge of the dissociation constants of the enzyme urease. It is evident from table 14, that k_a and k_b appear to be about 1.3×10^{-6} and 2.2×10^{-5} or even higher.

The dissociation constants of carbonic acid [1]) and ammonia at 27° are respectively 4.4×10^{-7} and 1.9×10^{-5} [2]).

The approach of these constants to those of urease is in a line with the author's view [3]) that enzymes generally contain in some active state the same molecule, which is liberated or acted upon by them.

Ammonium-carbonate + carbonic acid as a buffer-mixture.

In the beginning of this study it soon became clear to the writer, that the commonly accepted statement as to the accelerating action of CO_2 was not only not sufficiently borne out by experiment, but, as a matter of fact, might be totally erroneous.

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[1]) MICHAELIS und RONA, Biochem. Zeitschr. 1914, 67, 182.
[2]) LUNDEN, Affinitätsmessungen an schwachen Saüren und Basen.
[3]) BARENDRECHT, Biochem, J. 1913, 7, 549.

The action of urease on a solution of urea soon produces so considerable a lowering of the H-ion concentration, that the course of the hydrolysis is seriously checked. To regard the accelerating effect of a stream of CO_2, passed through this solution, as a proof of the specially favourable influence of CO_2 is an unnecessary assumption, as long as full account is not taken of the power, CO_2 has to compensate the depression of the H-ion concentration. This was not done by previous authors.

It was, however, known, that nature often makes use of bicarbonates and carbonic acid as well as of phosphate mixtures as buffers to maintain the necessary constancy of the true reaction in the living cell. The buffer action of bicarbonates in blood is a case in point, which has attracted much attention of late.

Before reaching the point of view, that the urease radiation is only absorbed by the substrate urea and the H-ions, the author assumed, that the products of the enzyme-action -- here ammonia and carbonic acid -- also absorbed the radiation to some extent and in this way interfered with the rate of hydrolysis.

At the same time it was taken into consideration, that by passing a continuous and abundant stream of CO_2 through a urease solution containing much ammonium-carbonate and not too large an amount of urea, the H-ion concentration might easily be maintained constant; for generally the true reaction of a solution of a bicarbonate, saturated with carbonic acid, is not changed by some variation in its concentration.

It was therefore that in 1915 and 1916 a considerable amount of experimental work was carried out with ammonium-carbonate and carbonic acid as buffer-mixture, a short account of which will now be recorded and explained by the theory afterwards developed.

The ammonium-carbonate employed was KAHLBAUM's Ammonium-carbonat, "zur Analyse mit Garantie-Schein".

By dissolving ammonium carbonate in water, as FENTON [1]) has shown, an equilibrium of ammonium-carbonate and ammonium-carbamate is obtained. FENTON's method of estimating both these compounds and urea in one solution by the use of sodiumhypochlorite and sodiumhypobromite was tried by the present author with a view to establish what was the original product of the hydrolysis of urea by urease.

The velocity with which both ammonium-carbonate and ammonium carbamate tend to equilibrium, is, however, too great. These efforts

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[1]) Proc. Roy. Soc. 1886. 39. 386.

were stopped the sooner as the question of what is the original product of change is not of much importance in these experiments. The change of carbamate to carbonate is generally quicker than the enzyme action and the carbonic acid converts all carbamate as well as carbonate into bicarbonate.

The powdered ammonium carbonate had practically the composition NH_4HCO_3. A solution of ammonium carbonate ($= 2 \%$ urea) will therefore mean in this paper a concentration of about $2 \times 2,63 \%$ ammonium carbonate.

The required amount of Soja-meal was digested at $27°$ with a solution of ammonium carbonate, through which a stream of carbonic acid was maintained during about one hour. After mixing with some kiezelgur a clear filtrate was very easily obtained, only slightly opalescent, if large quantities of Soja-meal had been used.

It is obvious, that the electrometric estimation of p_H is impossible in a solution of ammonium carbonate, which is to be kept saturated with carbonic acid. The much less accurate colorimetric method had therefore to be applied here. By using Tropaeolin 00 in order to give the SÖRENSEN phosphate solutions as nearly as possible the same colour as the ammonium carbonate extract of Soja-meal and kiezelgur and with rosolic acid as indicator, the p_H of an ammonium carbonate solution ($= 2 \%$ urea) with $1,36$ g. of Soja per 100 c.c., through which carbonic acid had been passed at $27°$, could be estimated to be about $7,0$. By adding ammonium carbonate ($= 0,5 \%$ urea) and passing carbonic acid again no distinct shifting of the p_H was observed.

As will be seen, no great accuracy is required in these experiments, where $\dfrac{\dfrac{a}{nc}}{0,434}$ is so much larger than above in the phosphate mixtures, that the curves all approach to straight lines.

As types of the numerous experiments only the following will be recorded here.

In a round bottomed flask of $\frac{3}{4}$ Litre, placed in a waterbath of $27°$, $15,125$ g. of ammonium carbonate, dissolved to 250 c.c., and 6 g. of Soja-meal were introduced. A few drops of octylalcohol were added to prevent foaming.

The carbonic acid from a steel cylinder was first passed through a narrow copper tube of about 150 c.m. length, placed in the bath and then through two wash-bottles, filled with water, also in the bath of $27°$. The stream of carbonic acid, in this way brought to the required temperature and saturated with watervapour, was passed

through the mixture in the flask for one hour, after which a rapid filtration with 2 g. of kiezelgur through a pleated filter gave a clear filtrate.

175 c.c. of this liquid were introduced into a similar round bottomed flask, closed by a rubber stopper, carrying two glass tubes, one of which, reaching to the bottom, admitted the carbonic acid, while the second short one was connected with a tube, filled with 10 c.c. of $H_2SO_4 \frac{1}{5} N$, to allow an estimation of the ammonia, which might have been blown over.

After saturation with carbonic acid the current was stopped, the controlling tube with H_2SO_4 was exchanged for another, the stopper of the flask was lifted a moment and 25 c.c. solution, containing 1 g. of urea were quickly introduced. This solution had been brought before to 27° in the same bath. After replacing the stopper and again admitting the carbonic acid the reaction was allowed to proceed at constant temperature and constant p_H and its progress measured from time to time by interrupting the current of carbonic acid for a moment, taking out a sample of 5 c.c. with a pipette and running this quickly into 25 c.c. of $H_2SO_4 \frac{1}{5} N$. After dilution with some water the contents of this flask were boiled to expel the carbonic acid and titrated with $NaOH \frac{1}{10} N$ and lacmoid (or later with Sodium alizarin sulphonate) as indicator. Owing to phosphate and proteins of the Soja, this titration was not very sharp, leaving an uncertainty of one or two drops of $NaOH \frac{1}{10} N$.
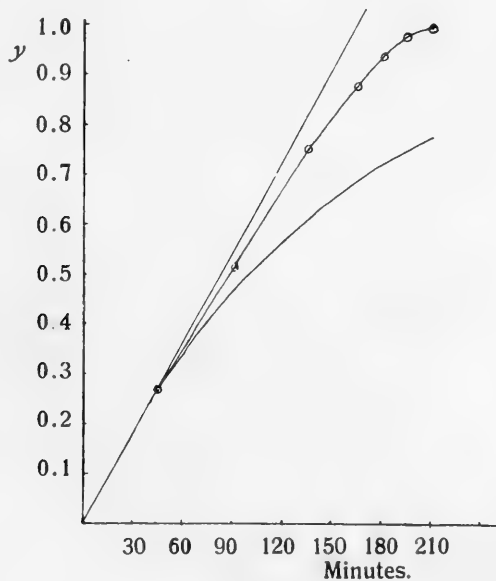
Fig. 5.

The ammonia in the original 175 c.c. solution was estimated in the same way as well as the small quantities, which might have been blown over with the CO_2 in the controlling tubes.

The results are represented in table 15 and in fig. 5, in which for the sake of comparison also the straight line and the logarithmic curve for $log \dfrac{1}{1-y} = kt$, are drawn, both through the origin and the first point, determined for y.

TABLE 15.

3 gr. of Soja on 286 c.c.
ammonium-carbonate ($= 2\%$ urea)

0.5 % urea $\qquad\qquad$ $p_H = 7$, hence $\dfrac{nc}{0.434} = 0.1$

t (minutes)	y	$m = \dfrac{0,1\ log\frac{1}{1-y}+0,5y}{t}$	$k = \dfrac{log\frac{1}{1-y}}{t}$
45	0.269	0.0033	0.0030
90	0.514	0.0032	0.0035
135	0.746	0.0032	0.0044
165	0.869	0.0032	0.0054
180	0.931	0.0032	0.0064
195	0.97	0.0033	0.0078
210	0.984	0.0032	0.0085

Repeated on many different ways these experiments always produced similar results.

For instance: Febr. 3rd, 1916. 3 g. of Soja extracted with 200 c.c. of ammonium carbonate solution.

A row of test tubes, each with 10 c.c. of filtrate and one drop of octylalcohol in the bath at 27°. Each tube connected with a wide tube (over the rim of the bath), containing 25 c.c. of $H_2SO_4 \frac{2}{5}$ N and some water. Hence current of CO_2 first passing test-tube and then wide absorption-tube. 1 c.c. of a 2,75 % solution of urea, out of flask in the same bath, added to each test-tube. Reaction stopped, without opening tubes or loosing connections, by running 25 c.c. of saturated potassium carbonate solution into test-tubes and blowing over the ammonia during the whole night. Next day titrated directly in the wide tube with NaOH $\frac{1}{10}$ N and sodium alizarin sulphonate as indicator. Two test-tubes with 10 c.c. of extract, without urea, treated in the same way.

TABLE 16.
3 g. of Soja on 220 c.c.
ammonium-carbonate (= 2 % urea)

0.25 % urea		$pH = 7$
t (minutes)	y	$m = \dfrac{0{,}1 \; log \dfrac{1}{1-y} + 0{,}25 \, y}{t}$
40	0.495	0.0038
60	0.685	0.0037
70	0.800	0.0039
80	0.876	0.0039
90	0.936	0.0039
95	0.945	0.0038
100	0.968	0.0039
105	0.974	0.0038
110	0.985	0.0039

These results show clearly, that the formula $\dfrac{nc}{0{,}434} log \dfrac{1}{1-y} +$
$+ ay = mt$ represents equally well the course of the reaction in urea solutions of far greater concentrations than above in the phosphate mixtures.

The nearly straight line, found generally in the hydrolysis of urea by urease, when a is not small, or at any rate large in comparison with $\dfrac{nc}{0{,}434}$, is equally well in accordance with the radiation theory as the logarithmic curve, the ordinary representation of the law of mass action, predicted by the same theory for dilute urea solution, if c is relatively large.

Initial velocity of urease action in urea solutions of different concentration.

Using phosphates as buffers it is, as shown above, impossible to study the course of the reaction in urea solutions, whose concentration exceeds about 0,02 %. If, however, we allow the same quantity of enzyme to act under the same conditions on urea-solutions of different concentration only to such an extent that no more than about 0,02 % urea concentration is hydrolysed, the phosphate mixtures can maintain a constant p_H in these initial periods of the process.

The experiments on this line were all arranged in the following manner :

A flask of 250 c.c. was filled to the mark with a solution of a mixture of Na_2HPO_4 2 aq and KH_2PO_4, calculated to produce a concentration of phosphate of $8^0/_0$ during the reaction. A small quantity of Soja-meal was added, mixed with this solution, and the flask was left for one hour in the bath at 27°. After addition of kiezelgur (the same weight as that of the Soja-meal) the solution was rapidly run through a pleated filter. From the perfectly clear filtrate portions of 10 cc. were introduced into test-tubes (as above) and placed in the same bath, in which a series of stoppered flasks with urea solutions were brought to 27°. As 2 cc. of these urea solutions were to be added to 10 cc. of enzyme-extract, all the urea-solutions had 6 times the required final concentration. The three highest concentrations of $4^0/_0$, $6^0/_0$ and $8^0/_0$ were obtained by preparing a solution of 4.8 g. of urea to 10 cc. and bringing 1 cc. of this with 1 cc. of water into the $4^0/_0$ tube, 1.5 cc. with 0.5 cc. of water into the $6^0/_0$ tube and 2 cc. into the $8^0/_0$ tube.

The reaction was allowed to proceed for a fixed time, usually 2 hours, after which the NH_3 formed was estimated by connecting the tubes with wider ones, into which had been brought 10 cc. of H_2SO_4 $\frac{1}{50}$ N and some water, running 25 cc. of saturated potassium carbonate and a drop of octylalcohol into the reaction-tube and passing a current of air for two hours.

The p_H was determined with the electrometer in 10 cc. phosphate-enzyme-solution $+$ 2 c.c. water at 27°.

The quantity of Soja-meal was usually 0.2 gram. Only at the lowest p_H more enzyme and different reaction times had to be taken. The results are then reduced to 0.2 g. of Soja and 120 minutes. (See tables 17 and 18 on following page).

The conclusions, to be drawn from these results, are the following:

The amount of action, produced under the same conditions, as to temperature and p_H, by the same quantity of urease in urea solutions of different concentrations becomes never really constant, not even in highly concentrated solutions.

The higher the acidity of the solutions, the more the amount of action increases with increasing concentration.

These facts are in agreement with the fundamental formula

$$- dx = m \frac{x}{x + nc} dt$$

For the initial velocity, when x is still equal to a, this formula gives the mathematical expression

$$- \frac{dx}{dt} = m \frac{a}{a + nc}$$

TABLE 17.

c.c. NH_3 $\frac{1}{50}$ N, formed in 120 minutes in 12 c.c.

Concentration urea a	$pH=$ 5.83	$pH=$ 6.68	$pH=$ 6.81	$pH=$ 6.89	$pH=$ 7.14	$pH=$ 7.47	$pH=$ 7.83	$pH=$ 8.10
0.03	0.068	0.58	0.95	1.2	1.65	3.2	3.2	2.9
0.05		0.9	1.4	1.7	2.25	3.45	3.75	3.2
0.08	0.164	1.3	1.9	2.3	2.7	4.05	3.55	3.2
0.1	0.21	1.6	2.15	2.5	3.—	4.15	4.1	3.4
0.2	0.375	2.3		3.4	3.55	4.65	4.3	3.7
0.5	0.85	3.3	3.9	4.3	4.1	5.—	4.5	3.8
1.—	1.5	3.9	4.5	4.65	4.3	5.05	4.25	3.9
2.—	2.75	4.45	4.9	5.2	4.5	5.15	4.75	4.1
4.—	3.2	4.8	5.15	5.4	4.45	5.25	4.6	3.9
6.—	4.15	4.85	5.2	5.3	4.45	4.85	4.35	3.65
8.—	4.65	4.8	5.—	5.15	4.25	4.6	4.—	3.25

TABLE 18.

Values of:

$$m = \frac{\dfrac{nc}{0,434} \log \dfrac{1}{1-y} + ay}{t} \qquad \text{or:} \qquad m = -\frac{dx}{dt} \left. \frac{x+nc}{x} \right]^{x=a}$$

multiplied by 1000.

Concentration urea a	$pH=$ 5.83	$pH=$ 6.68	$pH=$ 6.81	$pH=$ 6.89	$pH=$ 7.14	$pH=$ 7.47	$pH=$ 7.83	$pH=$ 8.10
0.03	0.068	0.103	0.135	0.153	0.140	0.23	0.174	0.139
0.05		0.114	0.142	0.157	0.160	0.19	0.181	0.144
0.08	0.066	0.128	0.150	0.168	0.160	0.20	0.161	0.140
0.1	0.067	0.136	0.153	0.166	0 167	0.20	0.184	0.147
0.2	0.066	0.143		0.181	0.172	0.21	0.185	0.157
0.5	0.08	0.165	0.184	0.199	0.184	0.21	0.189	0.159
1.—	0.102	0.178	0.194	0.199	0.182	0.21	0.177	0.163
2.—	0.152	0.185	0.208	0.220	0.190	0.22	0.198	0.171
4.—	0.154	0.205	0.218	0.226	0.186	0.22	0.192	0.163
6.—	0.19	0.205	0.219	0.221	0.186	0.20	0.181	0.152
8.—	0.20	0.203	0.209	0.214	0.177	0.19	0.167	0.135

If nc is large, compared with a, the initial velocity is small; a larger a gives a greater velocity. On the other hand, if nc is small, then even for low urea concentrations $\dfrac{a}{a + nc}$ is not small and will sooner approximate to a constant value.

The values of m were calculated in the tables, either, when y had an appreciable value, from the integrated equation, or from the differential equation for the initial velocity as soon as the urea concentration was high enough to make these equations give the same value.

The inconstancy of m will now be shown to afford favourable evidence to the radiation theory.

For in surveying the columns which give the c.c. $NH_3\,\frac{1}{50}\,N$, formed in equal times of action, a remarkable feature will be observed.

For low p_H these values increase continually from 0.03 up to 8 $^\circ/_\circ$ urea concentration.

For higher p_H there is first an increase and then, in the most concentrated urea solutions, a decrease.

This is exactly, what the theory would lead us to expect.

A urease particle being the centre of a sphere of action and the action in this case producing an alkaline substance, the H-ion concentration around the enzyme particle will be lowered and kept low by the enzyme action itself. This process will be negligible in dilute urea solutions, but in concentrated ones, where the sphere of action is concentrated into a small volume, a marked diminution of the H-ion concentration may be expected.

Bearing in mind the dependence of urease activity m on p_H (see Fig. 3), it will be evident, that in solutions of low p_H a decrease of the H-ion concentration around the enzyme particles, i.e. a diminution of c, means a rise of m. Hence for two reasons considerably more action is found here in high urea concentrations.

For, besides the increase of $\dfrac{a}{a+nc}$, there is also an increase in m, because the p_H, though constant as far as can be estimated in the solutions as a whole, is increased in the small sphere around the enzyme, to which the action is confined.

If p_H is not very low, the production of an alkaline substance around the enzyme particle may raise p_H above the optimum in these phosphate solutions. Hence in the concentrated urea solutions of a p_H near or above this optimum the p_H may soon be raised so far, that m is diminished.

Astronomy. — *"Investigation of a galactic cloud in Aquila."* By
Dr. A. PANNEKOEK. (Communicated by Prof. W. DE SITTER).

A communication to the Meeting of this Academy on
Dec. 8, 1911, described how, by means of some photographs,
it is possible to obtain data about the increase of star-density with
decreasing limiting magnitude. There it was stated already that
Prof. HERTZSPRUNG of Potsdam, by means of the Zeisstriplet of the
Astrophysical Observatory, had made some photographs (of the
galactic cloud N.W. of γ Aquilae), in order to test the method.
Various circumstances, however, prevented a final discussion of these
plates until quite recently.

The plates are 20×20 cm., the centre lies near χ Aquilae, and
the region that was photographed is 6° square. The plates immediately
used for this purpose are:

Nr. 328 Sept. 2 1910 Expos. 600, 600, 190, 60, 19, 6, 2 sec. (plate A)
Nr. 329 Sept. 2 1910 Expos. 1900, 1900 sec. (plate B)
Nr. 1260 Aug. 24 1911 Expos. 40^m, Halbgitter North (plate C_1')
Nr. 1261 Aug. 24 1911 Expos. 45^m, Halbgitter South (plate C_2')

As for the counting of plates A and B no reseau was printed
on the plates themselves, a reseau of $6^2/_3$ mm. interval was photo-
graphed on a separate glassplate instead, which reseau-plate, during
the counting, was firmly clasped to the counting-plates.

1. *The countings.* On plate A were counted in each square firstly
the numbers of stars with only 2 equal images, secondly those with
moreover a 3rd image, (190^s exp.) thirdly those with 4 images, (a
still visible image therefore for 60^s), those with 5, and with 6 images.
The respective limiting magnitudes differ about 1 magnitude; accord-
ing to some provisional comparisons with a photograph of the North
polar region they amounted to 13,0 . . . . . 9,0. The uncertainty and
the subjective differences of conception so common in star-counting,
the faintest star-images not being discernible from casual spots in
the plate, are practically done away with here, as every star must
present two equal images at a known distance, or as a faint image
must present itself at a given spot near the brighter images. Yet
this does not do away entirely with the uncertainty in counting;

TABLE I. Number of stars.

I

121	98	123	97	83	113	100	112	127	118
35	36	44	27	24	44	33	46	51	34
18 1	15 5	19 8	17 7	11 5	17 7	18 7	27 11	22 13	15 9
1 0	2 0	5 1	5 1	1 0	0 0	2 0	3 1	6 2	1 0
135	88	64	96	101	96	84	107	85	94
40	34	28	38	36	28	24	46	31	37
17 7	14 3	17 8	13 6	13 5	13 5	12 8	14 6	20 5	13 2
1 0	1 0	3 0	4 0	2 2	1 0	5 2	4 2	2 0	1 0
83	96	97	123	115	91	90	90	77	111
27	33	27	36	40	28	34	35	26	44
14 6	15 6	12 5	20 7	16 8	15 6	20 11	21 7	13 7	21 8
2 0	1 1	4 0	3 0	3 2	4 1	5 1	5 2	3 1	1 0
76	76	102	105	77	87	95	120	144	117
25	23	49	32	35	49	35	35	47	53
13 4	12 4	25 8	14 6	19 8	19 8	15 6	14 6	16 5	25 13
0 0	1 0	5 2	2 1	3 1	3 1	0 0	1 0	0 0	4 1
52	87	76	94	59	69	92	103	97	127
27	30	23	44	30	30	34	40	46	39
18 8	12 4	9 3	19 8	18 10	13 7	21 8	18 8	21 12	18 9
3 0	2 0	0 0	2 1	4 3	1 0	6 1	4 1	3 1	5 0
52	78	92 IV	72	84	82	111	110	84	118
18	25	31	22	33	39	32	33	34	40
9 3	8 4	9 3	10 5	19 6	20 7	17 7	21 5	16 6	11 3
1 0	2 0	2 0	1 0	1 0	2 1	3 2	2 0	2 0	0 0
55	73	88	55	58	99	95	117	106	88
13	21	30	16	21	35	49	41	55	36
8 3	11 2	10 4	4 1	13 7	16 9	25 10	15 5	24 9	17 8
2 0	1 0	1 0	0 0	3 0	5 2	4 1	2 0	4 2	2 1
45	52	54	19	28	72	89	88	87	94
20	25	25	12	10	24	29	34	32	27
9 6	10 2	12 5	6 0	5 0	12 6	15 5	20 6	10 2	12 3
2 1	1 0	2 0	0 0	0 0	3 0	3 0	2 0	1 0	2 1
53	51	38	38	21	29	84	63	61	71
16	10	10	9	5	9	26	35	33	30
9 3	6 3	6 5	5 2	2 0	5 1	14 8	16 9	15 7	14 6
3 2	2 2	1 0	1 0	0 0	1 0	2 2	5 0	4 1	5 2
39	24	35	53	34	39	39	60	46	61
19	13	8	15	11	15	18	30	20	31
12 1	8 2	6 4	8 2	6 3	10 4	8 1	15 8	14 5	17 9
0 0	1 0	1 0	0 0	2 1	2 1	1 0	2 0	2 1	3 0

III (left), II (right), IV (right), V (left)

on plate B some of the denser galactic regions are as it were dotted with scarcely perceptible spots, so that it often seems entirely arbitrary whether some of them are to be considered as belonging together, and to be counted as stars. In deciding whether a scarcely visible 3rd or 4th image existed alongside of the brighter images, the subjective certainty was considerably greater.

In the case of the brighter stars another uncertainty presented itself. It sometimes happened that of some star, which in the large images was decidedly fainter than another, more faint images could nevertheless be discerned, as here the fainter images were small and sharp, and with the others they were large and diffuse. This is caused by the uncommon achromatisation of the Zeisstriplet [1]), which renders the yellow stars large and hazy, and the white stars bright and small. This circumstance, which may be of use in deciding the colour of such weak stars, often rendered the counting troublesome; as a rule the visibility of the weakest image was taken as a criterion for the classifying.

The region counted comprises 100 squares (in AR. of -7 to $+3$, in decl. of $+5$ to -5). The centre of the plate lies on $279°30' + 11°30'$; the side of each square is $15',28$, so the surface is $0,0649 = {}^1/_{15,41}$ square degrees. The cornerpoints of the region explored are situated at

$$277°40'6+12°44',8; \quad 277°41',6 + 10°12',4; \quad 280°17',0 + 12°46',3;$$
$$280°16',5 + 10°13',6.$$

The countings have been executed by means of the microscope of the Repsold-apparatus for rectangular coordinates at the Leyden observatory, fitted out with the weakest ocular; the enlargement was tenfold, rather too strong for the purpose. The results of the countings have been collected in Table I; each square contains successively the number on plate B, the number on plate A, the numbers on A with at least 3 and 4 images, and the numbers on A with at least 5 and 6 images.

2. *The scale of magnitudes.* In order to find the limiting magnitudes for which these numbers stand, the magnitude of a number of stars had to be ascertained. This part of the investigation presented the greatest difficulties, as it had to be effected with somewhat

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[1]) The focal distance is minimum for 394 $\mu\mu$ (HERTZSPRUNG A. N. 4951. Vol. **207**. 88).

primitive means. To obtain a comparison-scale a portion of a photograph of Coma Berenices was cut out, containing side by side exposures of 12, 15, 19, 24, 30, 38, 48, 60, 76, 95, and 120 seconds, which means 11 images of every star, increasing 0^m, 2 in magnitude. By pressing this plate to the back of plate A or B, film against film, and comparing with an ocular enlarging 5 times, each star on A or B could be inserted by means of eye-estimate between the terms of the scale. The numbers of the scale-values represent the approximate magnitudes of stars that would have the same images on plate B.

By means of this scale in a number of regularly distributed squares the magnitude of all the stars distinctly visible on plate B was estimated and the like on A for all clearly visible and measurable images. Thus can be found the differences in magnitude between the various exposures, expressed in the provisional scale. To express the unity of this provisional scale in the absolute scale of magnitudes, two strips, North and South, were measured on either plate C in such a way as to leave each strip on the one plate entirely covered by the Halbgitter, and on the other quite free. By deducing from this the difference in magnitude of the images with and without the Halbgitter in the provisional scale and comparing it with the known absorption-coefficient of the Gitter, one can find the reduction to absolute scale. By means of a few stars of known magnitude the absolute magnitude can then be deduced.

The execution and reduction of the measurements showed that in case of the more brilliant stars with large images there existed systematic differences, that rendered a further use of them undesirable. With the fainter stars of the scale other errors presented themselves. The smaller images showed as somewhat irregular spots, and neither did these always differ 0^m,2 in magnitude. This may be caused partly by local differences of sensitiveness and a not wholly regular spreading of the silver-grains, which influence the look of these small faint spots, partly in the accidental coinciding of scale-images with images of other invisible stars. It proved necessary therefore, to ascertain separately the magnitude of all images of the scale that were often used. This was done by estimating them between the images on a polar plate, likewise following each other with a theoretical interval of 0^m,2; as each scale-image was inserted in various polar-star series, the errors of these series passed into the magnitudes of the scale to only a very slight extent. Thus for the magnitude of the faintest (0) up to the brightest image (10) of the stars w, s and r we found:

	0	1	2	3	4	5	6	7	8	9	10
w		invisible			14,4	14,15	14,0	13,8	13,6	13,4	13,2
s	14,2	14,05	13,9	13,85	13,45	13,15	13,0	12,85	12,7	12,4	12,25
r	13,25	13,0	12,8	12,5	12,25	11,9	11,75	11,75	11,5	11,35	11,15

These values were made use of in order to deduce the magnitude of the star-images in the squares on plate B and A: the shorter exposures give magnitudes decreasing by about 1^m, from which the difference in magnitude of the successive exposures B, A_1, A_2, A_3, may be deduced.

Classifying these differences according to magnitude, we find:

B	A_1	$B\text{-}A_1$	corrected	A_1	A_2	$A_1 \cdot A_2$	corrected
11,40	12,32	0.92(18)	0.98	11,46	12,40	0,94(5)	1,01
11,88	12,76	0,88(17)	0,96	11,85	12,81	0,96(11)	1,04
12,41	13,35	0,94(30)	0,91	12,30	13,49	1,19(17)	1,15
12,70	13,84	1,14(18)	1,00	12,76	13,95	1,19(17)	1,03
			0,95(83)				1,07(50)

A_2	A_3	$A_2\text{-}A_3$	corrected
12,28	13,35	1,07(8)	1.05
12,81	14,02	1,21(11)	1,04
			1,04(19)

The differences are not merely accidental; the fact that with all of them the last value is the greatest, proves that the scale is not yet wholly homogeneous. By successive approximations the following deviations from an evenly running scale were found -

11,42— 12,32	—0,06	12,36—13,35	+0,03
11,87 —12,73	—0,10	12,75—13,86	+0,15

These are accounted for by the following corrections to the scale:

11,2 --11,8	0	13,0	+ 0,07
12,0	+ 0,02	13,2	+ · 05
12,2	+ 04	13,4	+ 03
12,4	+ 07	13,6	00
12,6	+ 08	13,8	-- 04
12,8	+ 09	14,0	— 08

By introducing these corrections, we get for the difference in magnitude $B_1 - A = 0,95$; $A_1 - A_2 = 1,07$; $A_2 - A_3 = 1,04$. For the shorter exposures only the brighter stars could be used; they gave the result of $A_3 - A_4 = 1,16(7)$; $A_4 - A_5 = 1,09(14)$. The mean error of 1 determination of magnitude is $0^m,14$.

To this same scale were compared a number of stars in the N. and S.-strip on the Halbgitter-plates C_1 and C_2. Here the result was:

S.-strip: ordinary image C_1 — weakened image C_2 =
$$= 13,78 — 11,63 = 2,15 \ (75)$$
N.-strip: ordinary image C_2 — weakened image C_1 =
$$= 13,78 — 11,48 = 2,30 \ (38)$$

This gives for the absorption of the Halbgitter in unities of the provisional scale 2,22. In absolute scale according to the statement of Prof. HERTZSPRUNG at Potsdam there was found for this absorption 1,963 magn. All the intervals deduced here must therefore be multiplied by the factor 0,884, in order to express them in magnitudes (this means that a 10 times larger exposure gives a gain of 1,77 magn.). Then they are:

$$B — A_1 = 0^m,84; \ A_1 — A_2 = 0^m,95; \ A_2 — A_3 = 0^m,92;$$
$$A_3 — A_4 = 1^m,02; \ A_4 — A_5 = 0^m,96.$$

In order to express also the magnitudes themselves in absolute scale, 16 of the most brilliant stars were used, which are contained in the "Göttinger Aktinometrie"; from the magnitude of their 5th and 6th image was found:

$$m — 11,55 = 0,884 \ (\text{prov.} \ m — 11,55).$$

3. *The limiting magnitude.* The difference in limiting magnitude will be equal to the differences in magnitude found here for the same stars at various exposures, provided the conditions under which the observations are made be absolutely identical. On the plates B and A_1 each star presents two equal images; all the double images therefore that are at all discernible are counted. With regard to the exposures A_2 A_3 A_4 and A_5 on the other hand, a faint, scarcely distinguishable image must be looked for, in a given spot by the side of brighter images. If the chance that by the fluctuations in the conditions a star-image near the limit of visibility can be just discerned $= a$, then the chance that two equal images are both visible $= a^2$; in this case therefore more stars remain invisible. With such counting as on B and A_1 therefore fewer will be counted, systematically, than with the method employed for A_2 etc. For the difference in limiting magnitude $A_1 — A_2$ the difference in magnitude found above can therefore not be used.

In order to find this difference during the counting of the plates A charts had already been drawn of those squares, where later on the magnitude of all clearly visible stars was to be ascertained, on which charts were indicated all the stars showing 2, 3, 4, 5 and 6 images. We must now find what magnitude, measured on B, forms

the limit between the stars that are visible on A and those that are invisible; this is the limiting magnitude for A_1. In the like manner we find out what magnitude forms the limit between the stars with 2 and with 3 images on A; this is limiting magnitude for A_2. From the first follows, with the difference B—A_1, the limiting magnitude B, from the second follows, in the same manner, the limiting magnitude for A_3, A_4, and A_5.

In the application this method proved to involve many difficulties as yet, as the magnitudes of the stars visible and invisible on A, as well as those of the stars with 2 and 3 images, extend far the one over the other, and are moreover irregularly distributed. If m_1 is the magnitude measured on B, differing from the real magnitude m by the unequal sensibility of the plate and by errors in the counting, and if the magnitude on the counting plate, likewise diverging from m, is m_2, then the star will be visible or invisible, according to whether $m_2 <$ or $> m_0$, the limiting magnitude. If the differences $m_1 - m$ and $m_2 - m$ follow the law of errors and if the stars are divided regularly over the various magnitudes, there are two criteria for the ascertaining of m_0:

1. for $m_1 \gtrless m_0$ the number of invisible stars is $\gtrless$ the number of visible ones; m_0 therefore is that value of m_1, for which 50 % of the stars is visible, 50 % invisible;

2. for $m_1 \gtrless m_0$ the total number of brighter, invisible stars is $\gtrless$ the total number of fainter, visible stars; m_0 therefore is that value of m_1 above which appear a number of visible stars, equal to the number of invisible ones below.

Now the number of stars for greater m increases; the average m, corresponding with a measured m_1, will consequently be somewhat larger than this latter; the limiting magnitude found according to the first criterion, needs a positive correction, which is somewhat diminished, however, by the differences $m_2 - m$. On the other hand by means of the 2nd criterion the correct limiting magnitude is found if the number of stars is a linear function of the magnitude m [1]).

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[1]) This can be proved in the following manner. The number of stars of real magnitude m that is measured on the one plate in magnitude m_1, and likewise the number that on the other plate shows the magnitude m_2, is respectively

$$f(m) \exp. (-h_1^2 (m_1 - m)^2) \, dm \, dm_1 \quad \text{and} \quad f(m) \exp. (-h_2^2 (m_2 - m_1)^2) dm \, dm_2$$

in which $f(m)$ represents the number of stars of the magnitude m; this $f(m)$ has the form $a + bm$.

If we pose:

$$\frac{h_1^2 m_1 + h_2^2 m_2}{h_1^2 + h_2^2} = m_3 \qquad \frac{h_1^2 h_2^2}{h_1^2 + h_2^2} = h^2$$

And if this function and the module of accuracy for magnitudes diverging 1^m may be considered as equal, the correction for both limiting magnitudes is equal with the 1st criterion, so that the difference in magnitude A_1-A_2 is correctly found also in this way.

In table II the 2nd and 3rd columns contain the numbers of stars with 0, with 2, with 3 images (n_1 n_2 n_3). In order to smooth the very considerable, accidental irregularities of these numbers, the total of every 3 consecutive numbers have been placed in the following columns (n_1^0 n_2^0 n_3^0). Column p shows how many percentages n_2^0 is of the sum total; where in the increase this amounts to 50 %, the limit lies between invisibility and two images; where in the decrease it amounts to 50 %, the limit lies between two and three images, according to the 1st criterion. Next to that stand the sums-total s of the fainter, visible, and the brighter invisible stars; the limiting magnitude, according to the 2nd criterion lies where these become equal.

From the values p_2 we find as limiting magnitude 13,67 and 12,54; to this must be added the corrections of page 1327, so that they become 13,65 and 12,62. From the 2nd criterion we likewise find

the number of stars having on the one plate the magnitude m_1, on the other m_2 becomes

$$f(m_3) \exp \cdot (-- h^2 (m_1 - m_2)^2) \, dm_1 \, dm_2.$$

If m_0 is the limiting magnitude, so that $m_2 \gtrless m_0$ means invisibility or visibility, then the number of invisible and the number of visible stars of the magnitude m_1 is given by:

$$dm_1 \int_{m_0}^{\infty} f(m_3) \exp. (-h^2(m_1 - m_2)^2) \, dm_2 \quad \text{en} \quad dm_1 \int_{-\infty}^{m_0} f(m_3) \exp. (-h^2(m_1 - m_2)^2) \, dm_2.$$

For $m_1 = m_0$ these two are not equal, in consequence of the factor

$$f(m_3) = a + b \, \frac{h_1^2 m_1 + h_2^2 m_2}{h_1^2 + h_2^2}.$$

The number of bright invisible stars, that have therefore $m_1 < m_0$. $m_2 > m_0$ and the number of faint visible stars that have $m_1 > m_0$ and $m_2 < m_0$ is

$$\int_{-\infty}^{m_0} dm_1 \int_{m_0}^{+\infty} dm_2 f(m_3) \exp. (--h^2 (m_1 - m_2)^2)$$

and

$$\int_{m_0}^{\infty} dm_1 \int_{-\infty}^{m_0} dm_2 f(m_3) \exp. (- h^2 (m_1 - m_2)).$$

These two double-integrals are equal, m_1 and m_2 being completely interchangeable here.

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13,72 and 12,63 or, corrected, 13,70 and 12,71. The difference in the limiting magnitudes B_1 and A_2 according to the first criterion is 1,03, according to the second 0,99; this, as we expected, is less than the difference in magnitude 1,07; yet they do not differ as much as might have been expected. The good concurrence of these two values is no proof for their accuracy, as they have been arrived at by means

TABLE II.

m	n_1	n_2	n_1^0	n_2^0	p_2	s_2	s_1
14.5	2		2				
14.45	0		6				
14.4	4		5		0		
14.35			5	1	17		
						1	
14.3	0	1	6	2	25		
						3	
14.25	5	1	8	3	27		
						6	
14.2	3	1	13	2	13		
						8	
14.15	5	0	16	1	6		
						9	
14.1	8	0	24	0	0		
						9	
14.05	11	0	36	3	8		
						12	
14.0	17	3	38	9	19		
						21	
13.95	10	6	48	18	27		
						39	
13.9	21	9	37	17	32		
						56	171
13.85	6	2	29	12	29		
						68	142
13.8	2	1	21	13	38		
						81	121
13.75	13	10	18	11	38		
						92	103
13.7	3	0	30	27	47		
						119	73
13.65	14	17	19	20	51		
						139	54
13.6	2	3	21	30	59		
						169	33
13.55	5	10	9	13	59		
						24	
13.5	2	0	9	26	74		
						15	
13.45	2	16	4	17	81		
						11	
13.4	0	1	3	21	88		
						8	
13.35	1	4	3	16	84		
						5	
13.3	2	11	3	16	84		
						2	
13.25		1	2	18	90		

m	n_2	n_3	n_2^0	n_3^0	p_2	s_3	s_2
13.2	6		12		100		
13.15	5		21		100		
13.1	10		24		100		
13.05	9		27	1	96		
						1	
13.0	8	1	31	5	86		
						6	
12.95	14	4	27	7	79		
						13	
12.9	5	2	26	8	76		
						21	
12.85	7	2	15	5	75		
						26	112
12.8	3	1	16	4	80		
						30	96
12.75	6	1	14	4	78		
						34	82
12.7	5	2	17	7	71		
						41	65
12.65	6	4	13	12	52		
						53	52
12.6	2	6	11	12	48		
						65	41
12.55	3	2	6	9	40		
						74	35
12.5	1	1	8	7	53		
						81	27
12.45	4	4	6	5	55		
						86	21
12.4	1	0	8	8	50		
						94	13
12.35	3	4	5	13	28		
						107	8
12.3	1	9	5	17	23		
							3
12.25	1	4	2	14	12		
							1
12.2		1	1	15	6		
12.15		10		16	0		
12.1		5		15	0		
12.05		0		5			
12.0		0					

of cognate methods. The irregular course of the numbers n_1^o n_2^o n_3^o that make up our material, renders it doubtful whether the value found is accurate up to 0,1. If we take the average 1,01, and for A_1 and A_2 13,71 and 12,70, we find for all limiting magnitudes (expressed in the provisional scale):

B 14,66; A_1 13,71; A_2 12,70; A_3 11,66; A_4 10,50; A_5 9,41.

When reduced to the real magnitudes, the limiting magnitude is therefore:

B 14,30; A_1 13,46; A_2 12,57; A_3 11,65; A_4 10,62; A_5 9,66

and the differences in limiting magnitude become:

0,84   0,89   0,92   1,03   0,96 magn.

4. Results. In the square that was examined the stars are not regularly distributed. The greatest density is found on the N. and W. sides; it seems as if two star-clouds, one from above, and one from the right, stretch into this region, divided by a region of less density, reaching towards the S.E. Below lies a triangular, very poor region. Herein as a kind of core, lies the three-armed void, which in the photographs of the Galaxy taken by MAX WOLF and BARNARD, shows like a black spot or hole[1]). On dividing the field into 5 regions of equal size, each of 20 squares, (the outlines of which have been indicated on Table I by means of thicker lines), so that I and II comprise the densest, III and IV the medium, and V the poorest region, we find for the numbers of stars:

	I	II	III	IV	V	Sum total	$\log N$	m	$\dfrac{d \log N}{dm}$
B	2169	2100	1571	1513	801	8154	3.099	14.30	
									0.52
A_1	746	787	601	584	279	2997	2.665	13.46	
									0.36
A_2	336	360	297	283	145	1421	2.341	12.57	
									0.43
A_3	136	142	127	116	48	569	1.943	11.65	
									0.39
A_4	55	51	49	47	22	224	1.538	10.62	
									0.63
A_5	14	13	12	9	7	55	0.928	9.66	

The values resulting herefrom for $\log N$, the amount per square degree, and for the gradient, are to be found for the entire square in the last columns, for the five minor regions in the following list.

The gradients for the entire region present a few irregularities. The differences between the last 3 values can be attributed to acci-

[1]) Compare e.g. MAX WOLF, Die Milchstrasse, Fig. 33 and 34.

$\log N$					$\dfrac{d \log N}{dm}$				
I	II	III	IV	V	I	II	III	IV	V
3.22	3.21	3.08	3.07	2.79					
					0.55	0.51	0.49	0.50	0.55
2.76	2.78	2.67	2.65	2.33					
					0.39	0.37	0.35	0.35	0.32
2.41	2.44	2.36	2.34	2.05					
					0.41	0.42	0.39	0.41	0.52
2.02	2.04	1.99	1.95	1.57					
					0.38	0.44	0.40	0.38	0.33
1.63	1.59	1.58	1.56	1.23					

dental irregularities or to errors, not so however in the case of the two former ones. This is proved by the fact that in all five regions the 2nd gradient is smaller, and the first larger than the others. To all probability the reason for the smallness of the second gradient must be attributed to the fact that the real difference in the limiting magnitudes is smaller still — so that the influence of overlooking the faintest stars on S and A_1 is yet stronger — than was ascertained and accepted above. On account of this therefore all the second gradients should be somewhat larger. The interval $B-A_1$, the first gradient, does not change in this case, as the countings on B and A_1 are absolutely similar.

The first gradient is larger than the others. Here then is manifest *the influence of the distant galactic condensations, which therefore is perceptible in the gradients only after the* 13,5th *magnitude.*

The fact that the gradients in region V do not essentially differ from those of the other regions, allows us to draw some important conclusions. This region must be considered as a weakened extension of the tripartite dark hole that forms its core. The cause of the lacking of stars in this hole, extends gradually weakening, over a wider region. As a first explanation we may admit that this cause consists in a local diminished space-density of the stars, so that there is an actual hole between and in the dense star-clouds that constitute the galaxy. In this case the nearer stars are not influenced thereby, so they must show no thinning, the brighter stars will be relatively more numerous than the faint ones, and the gradient must be smaller than in the denser regions. Of this the numbers show nothing; the stars from the 10th to the 14th magnitude are all diminished to an equal rate. This would imply that these brighter stars for the greater part belong to the galactic clouds themselves and are situated at the same great distance. This supposition, however, is excluded by the

value of the gradients between the 10th and the 13th magnitude.

A second explanation is the admittance of absorbing nebulous masses. If such nebulous matter should exist in the regions of the galactic condensations, only the more distant stars would be dimmed, and the phenomena would be the same as in the former case, a relative excess of brilliant stars. From the numbers found, it therefore becomes evident, *that the absorbing dark nebulous mass causing the tipartite hole, is so near as to dim also the majority of the stars of the 10th and 11th magnitude. It stands in no organic connection to the galactic clouds, being only accidentally projected against that clear background.*

5. *Comparison with other results.* Our former investigations [1] stated for the galactic region in Aquila a strong increase of the gradient up to far over 0,6. These results however cannot be immediately compared with the present ones, another scale of magnitudes having been used. The scale of Groningen Publ. 18 that was employed there, needs increasing corrections to reduce them to the visual Harvard scale; in order to obtainthe photographic magnitudes, belonging to *log N*, still increasing positive corrections have to be added, as the average colour-index increases for the fainter stars. [2] With these corrections we get:

	(m Gr. 18)	m vis.	m phot.	$log\ N$	$\dfrac{d\ log\ N}{dm}$ vis.		$\dfrac{d\ log\ N}{dm}$ phot.
1. B. D.	9.24	9.35	9.76	0.898			
2. C. d. C. Catal.	11.73	11.97	12.52	2.249	1—3	0.47	0.44
3. Epstein.	12.51	12.89	13.51	2.557	2—4	0.54	0.51
					3— 4	0.76	0.72
4. C. d. C. Chrt.	13.20	13.74	14.41	3.205	3—5	0.79	0.74
					4 5	0.82	0.76
5. Herschel.	13.90	14.65	15.39	3.948			

Here an increase of the gradient from the 13th magnitude (phot.) upward is perceptible; this therefore corresponds to the results now obtained. But the values of the gradients now obtained are consi-

[1] Researches into the structure of the Galaxy. Proceedings R. A. S., Amsterdam, June 25th 1910.

[2] P. J. van Rhijn. On the number of stars of each photographic magnitude. Publ. Groningen N°. 27.

derably less than those resulting from the former investigation (now 0,52 from 13,5 to 14,3, then 0.72 from 13,5 to 14,4) which clearly pointed to the presence of large, more distant star-condensations. Now the photographic scales are absolutely independent of one another, and therefore they are not perhaps immediately comparable. If e.g. the reduction-factor employed, 0,884, were somewhat too large, (so that a tenfold exposure would mean a gain of a little under $2 \times 0^m,884$) in the present investigation all, the m's and all their differences would become smaller, and the gradients larger. In how far this is actually the case cannot be ascertained with accuracy. In any case by means of these triplet-photographs we penetrated less deeply into the fainter stars than at the former investigation. When the project for these photographs was made it did not seem really difficult to penetrate further than HERSCHEL's gauges, the limiting magnitude of which then was found to be 13,9. On account of the scale-reductions since obtained, this purpose, as has now become evident, has not yet been accomplished. It would have required an instrument with a larger opening, or a far greater time of exposure.

In order to advance further, Prof. HERTZSPRUNG, at my request, made a few more photographs with the 80 cm. refractor at Potsdam. To immediately fix the scale of magnitudes on the plate, a coarse grating was placed before the objective, so that the central image is weakened $0,^m748$ and the 1st and the 2nd diffraction-image become $2,^m242$ and $3,^m317$ fainter than the central image. On a plate with the centre on 46 Aquila ($19^h37,^m5 + 11°57'$) on 0,343 square degrees 858 stars were counted, of which 101 present the first, and 24 the second diffraction-image. From this we find for

m_0	$m_0 - 2,24$	$m_0 - 3,32$
$log\ N$ 3,398	2,469	1,845

from which result the gradients $\dfrac{d\ log\ N}{dm} = 0,41$ and 0,58. This plate penetrates somewhat further than the Triplet, for from the comparison with the numbers round about 46 Aquilae that were found in Table I, there results $m_0 = 14,8$. Here the gradient from 12,6 to 14,8 proves to be only 0,41. The smallness of this amount is probably due to the fact that far fainter side-images were included than principal images, their place being accurately known. Here again it is evident, how easily, through dissimilarity of conditions systematic differences may occur in the amounts of stars counted, which render them useless for the deduction of gradients.

Another means of penetrating still further are the plates taken by FRANKLIN-ADAMS; according to CHAPMAN and MELOTTE they go below the 17th magnitude (photogr.), which is also proved by the numbers they give. For the galactic zone the number N for the magnitude 15,0 16,0 17,0 according to their original statements was 650, 1300, 2050; these numbers, on account of erroneous formation of mean values are too small, and later on Dr. CHAPMAN gave for the two former 840 and 1700 ($log N$ 2,92 and 3,23)[1] that is 29°/₀ and 31°/₀ more: if therefore we take the latter 33°/₀ larger, the number for 17,0 becomes $N = 2800$. The table of VAN RHIJN for these N gives the photographic limiting magnitudes 15,2 16,2 and 16,9, which proves that the stars up to 17,0 have been incompletely counted. From the values of N, deducted in Gron. Publ. 18 for HERSCHEL viz. $N = 175,6$ 373 1023 for the 3 zones 40—90, 20—40 and 0—20 galactic latitude, follows the photographic limiting magnitude for HERSCHEL 15,30 15,18 and 15,17. The countings therefore, indicated by CHAPMAN and MELOTTE with 17,0, penetrate $1\frac{1}{2}$ magnitude further into the faint stars than HERSCHEL's gauges.

The separate countings on plate 136 (A.R. $20^h,0$; decl. 15°) containing the region of Aquila, have been kindly put at my disposal by Prof. DYSON. For this plate the limiting magnitudes have not been determined photometrically, so that $\dfrac{d \log N}{dm}$ cannot be strictly deduced. If for the m the average values are taken, then we find (as the average of 6 regions, situated in the Galaxy in Aquila and Sagitta)

$$m = 14,4 \qquad 15,3 \qquad 16,3 \qquad 17,0$$
$$N = 965 \qquad 3445 \qquad 11883 \qquad 14310$$

$$\frac{d \log N}{dm} = \qquad 0,61 \qquad 0,53 \qquad 0,12$$

This last difference once more proves that CHAPMAN and MELOTTE have counted the faintest stars very incompletely, in these dense galactic regions even more so than elsewhere. Also in the other differences little is to be detected of the strong gradient that might have been expected from HERSCHEL's numbers. CHAPMAN has treated also the densest parts of the galactic zone separately, and finds for it:

$$\text{for} \qquad m = 13 \qquad 14 \qquad 15 \qquad 16$$
$$log N = \quad 2,63 \quad 3,07 \quad 3,37 \quad 3,60$$

[1] S. CHAPMAN. The number and galactic distribution of the stars. Table A Monthly Notices 78. p. 70.

Thus the gradients become 0,44 0,30 and 0,23. These numbers again show no trace of a spacial condensation in distant galactic clouds.

The contradiction that appears in all these results, and that has repeatedly disappointed the hope of penetrating further than HERSCHEL, can be summarised thus: *in the bright galactic clouds the Franklin-Adams plates show hardly any greater amount of stars than did the gauges of* HERSCHEL, although, as far as the average numbers are concerned, they go far deeper. On the region of plate 136 the countings of CHAPMAN and MELOTTE give 9340 stars per square degree, and HERSCHEL 7500, whereas the average of the entire galactic zone with the one surpasses 2800, and with the other only amounts to 1023.

It is not immediately clear what may be the cause hereof. The most plausible explanation is, that the countings of the faintest stars on the Franklin-Adams plates in the densest regions are far more incomplete than in other regions. Another explanation would be, that in the bright, dense galactic clouds the colour-index is higher, so that there the average of the stars would be redder than in the average of the galactic zone. In this case with countings on photographic plates, no matter how complete, we advance less than with visual countings by means of a telescope with a wide opening. So far therefore we cannot penetrate further into the depths of the galactic clouds than HERSCHEL did; our material reaches hardly any further than that collected by WILLIAM HERSCHEL more than a century ago. That nothing has been done during the whole of the 19th century to complete and correct his work, is doubtlessly due to the fact that the photographic method with regard to the counting of stars promised so much more, but has failed as yet to fulfill its promise. The numerous systematic differences which the photographic method involves, — the decrease of star-density towards the borders, the greater influence of atmospheric absorption, the variation in limiting magnitude — all this renders it extremely difficult, to deduce a homogeneous material from a photographic survey of the sky. If we consider, moreover, that the faintest stars, the main object of investigation, as an average have a higher colour-index, it becomes yet more evident how desirable visual countings with instruments of high power are for the study of the galatic condensations.

Chemistry. — *"On an Indirect Analysis of Gas-Hydrates by a Thermodynamic Method and its Application to the Hydrate of Sulphuretted Hydrogen"*. II. By Prof. F. E. C. SCHEFFER and G. MEYER [1]). (Communicated by Prof. BÖESEKEN.)

(Communicated in the meeting of March 29, 1919).

7. *Determination of the Three-Phase Lines* $SS_B G$ *and* $SL_2 G$.

A number of apparatus of the shape of fig. 3 was supplied with small quantities of water, which were introduced through C and conveyed to the widened part A by tilting the apparatus. These quantities of water were chosen so that the vessel A was filled with water for about a fifth part. Every apparatus was then in succession connected with a sulphuretted hydrogen apparatus in which the gas could be developed by the addition of drops of diluted sulphuric acid to a solution of acid sodium sulphide. The latter was obtained by saturating a solution of sodium hydroxide made free from carbonic acid with barite with sulphuretted hydrogen.

Before the preparation of the gas the wall of B and C, which was still damp with water, was dried by being heated at an air-pressure of 2 cm. of mercury, the bulb A being placed in carbonic acid and alcohol. Between the filling-apparatus and the apparatus C a T-piece was inserted for this purpose, which made connection with a waterjet pump possible. Then bulb A was filled for about two thirds with dry liquid sulphuretted hydrogen (the gas was led through a U-tube with P_2O_5 to prevent liquid from being carried along), after which the tube was fused to at C, and the cooling mixture was removed.

When the temperature was raised to room-temperature, the ice melted, and two layers were observed separated by a crust of sulphuretted hydrogen hydrate. In order to convert the mass as much as possible to hydrate, bulb A was carefully heated by immersion in a waterbath of over $30°$ (the quadruple point $SL_1 L_2 G$ lies at $29.5°$ [2])), till the hard crust had disappeared. Then the apparatus

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[1]) First communication, These Proc. **21**. 1204. (1919).

[2]) These Proc. **13**. 843. 1911). Table.

being continually shaken was cooled down to the ordinary tempe-
rature to make the action of the two layers as complete as possible
If any liquid sulphuretted hydrogen had been distilled over, it was
always poured back into A by tilting of the apparatus. When in
this way the cooling down to room-temperature had been achieved,
the apparatus was left for a few days to promote the action.

To make vapour pressure determinations bulb A was cooled in
liquid air, the apparatus was opened at C, and connected to the
tube D of the apparatus represented by fig. 4 by means of india
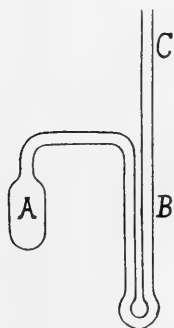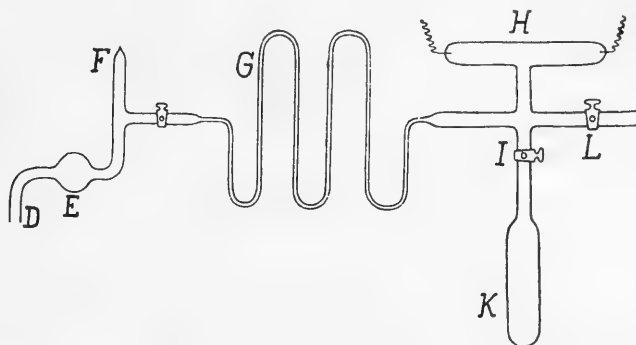
Fig. 3.   Fig. 4.

rubber. By exhaustion through tap L with a waterjet airpump the
sulphuretted hydrogen-air mixture was partially removed from B
and C (fig. 3); the rest of the gas was absorbed by the cooled
cocoanut carbon K by opening of I (after L had been shut). When
the gaseous sulphuretted hydrogen had entirely disappeared from the
apparatus, air was admitted, and the apparatus of fig. 3 was fused
to that of fig. 4 at D. Then the apparatus was again evacuated, the
liquid air round A was replaced by carbonic acid and alcohol, and
the sulphuretted hydrogen was sucked off through L. After the
liquid sulphuretted hydrogen had been removed from A by boiling,
the apparatus remained in connection with the waterjet pump for a
few hours more in order to remove the sulphuretted hydrogen ab-
sorbed in the solid substance as completely as possible. Then bulb A
was again placed in liquid air, the apparatus was completely evacuated
by the aid of the cocoanut carbon, air was admitted, tube F
was temporarily opened to convey mercury into E, and the whole
apparatus was exhausted again.

The mercury in E was freed from air by heating in vacuum.
After the mercury had been cooled, A was again placed in carbonic

acid and alcohol, and evacuated with the waterjet pump, afterwards with the carbon.

When after the evacuation with the cocoanut carbon tap *l* was closed, a gas pressure again appeared in the apparatus after a short time (GEISSLER tube *H*), and this was continually repeated. We shall discuss the cause of this phenomenon later on. When the gas that had generated in the apparatus, had been removed a few times, so that it might be assumed that the apparatus did not contain any more air, the mercury was transferred from *E* into *B* by tilting of the lefthand part of the apparatus (the glass spring *G* made this movement possible). The tap near *G* was now closed, and the apparatus was cut through between this tap and the glass spring *G*.

The lefthand part was connected by means of a rubber tube to a manometer one meter long, for the higher pressures three meters long. By a sucking pump, a tap that allowed contact with the outer air, and a tap that was connected with a cycle pump, the pressure of the air between *B* and the manometers could be regulated at will in the measurements. Hence tube *B* acts as a cut-off valve in the determinations; the difference of level in the manometer corrected for the difference of position in *B* yields the value of the three-phase pressure. In order to make it possible to determine the difference of level in *B* a glass scale graduated in millimeters was attached to the tube *B* by the aid of cork disks and copper wire. The determinations being carried out exclusively at temperatures below room temperature, only bulb *A* was placed in a bath of alcohol, which could be cooled down to definite temperatures by addition of solid carbonic acid; a stirrer ensured uniform temperature in the alcohol bath. The cut-off valve *B* remained continually in contact with the outer air.

During the slow heating of the alcohol bath it now appeared that already at low temperatures a rapid rise of pressure appeared, which could not possibly be attributed to decomposition of the hydrate. When the pressure had reached a definite value, the change with the temperature had greatly diminished again. This fact pointed to this that in spite of the exhaustion with the cocoanut carbon the hydrate had absorbed appreciable quantities of sulphuretted hydrogen, which were liberated already at temperatures of about — 50° C.

The exhaustion with the cocaonut carbon had, accordingly, not been sufficient to remove the absorbed quantity of sulphuretted hydrogen; prolonged evacuation is, however, undesirable, because as will appear later, the hydrate still possesses an appreciable tension of dissociation at — 80° C., and decomposition must, accordingly

take place in vacuum. Hence the appearance of this gas-absorption, and the pressure of dissociation which is not negligible at — 80° C. are the cause that the compound cannot be prepared in pure state in the way described above. These two phenomena have, however, no disturbing influence on the determination of the three-phase pressures, at least when the gas adsorption does not attain to too large amounts.

It is namely clear from the described phenomena that the gas-adsorption is no phenomenon of equilibrium; at higher temperatures, where the equilibria set in more rapidly, this adsorption soon stops; and the liberated sulphuretted hydrogen cannot influence the three-phase pressure (the three-phase equilibria are monovariant). Nor can a partial decomposition of the hydrate have any influence on the pressure of equilibrium.

Nevertheless a difficulty presents itself in these determinations. When the compound had absorbed no gas, a gas pressure could only appear on heating through decomposition of the compound into ice and gas; the observation of a gas pressure would then be a sufficient criterion that a three-phase pressure existed. In consequence of the said adsorption it is, however, possible that with increased temperature through liberation of gas a gas pressure occurs without any decomposition of the compound taking place. As the transformation of part of the compound into ice and gas cannot be directly observed, the possibility exists that pressures of two-phase equilibria compound-gas are measured instead of three-phase equilibria. It now appeared in the determinations that at lower temperatures no corresponding values were found for the pressure (the two-phase coexistences are divariant); at higher temperature the correspondence became, however, very good. This can, evidently, be accounted for in this way that the solid substance had absorbed different quantities of sulphuretted hydrogen, which were liberated on increase of temperature. When this released quantity of gas yields a pressure higher than the three-phase pressure, the decomposition of the compound cannot begin. Not until through increase of temperature the three-phase pressure rises so much that this becomes greater than the pressure caused by the liberated adsorbed gas, three-phase pressures occur. On account of the different adsorbed quantities this takes place for the different mixtures at different temperatures. In none of the experiments did the adsorption prove to be so great that the determinations of the three-phase pressures were rendered impossible. As was natural only the values in the neighbourhood of the quadruple point, where the correspondence was good, were used for the calculations. (See § § 8 and 9).

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8.   The Three-Phase Line Hydrate-Ice-Gas.

In the tables 1—3 the results have been recorded of three sets of observations. In the first and second columns of every table the temperatures and the corresponding three-phase pressures (in cm.) are given, the last have been reduced to mercury of $0°$ C. The third column contains the tensions corrected for the vapour tension of ice, the fourth and the fifth contain the differences in the BRIGG logarithms of the pressure and in the reciprocal absolute temperatures of the successive observations. The sixth column gives the value of $\dfrac{Q_1}{2.303\,R}$ calculated according to § 5; as in § 5 the calculation was made with Neperian, in tables 1—3 with ordinary logarithms, the modulus 2.303 occurs here in the denominator. The last column records the mean values of the last mentioned expression. The first value of P in table 3 is too high; it probably refers to the equilibrium hydrate-gas (cf. § 7). It is easy to see that the too small

TABLE 1.

t	P	$P(corr)$	$10^2 \Delta\, log\,P$	$10^5 \Delta\, T^{-1}$	$\dfrac{Q_1}{2.303\,R}$	mean
−25.85	22.4	22.35				
			12.929	9.74	1327	
−19.75	30.2	30.1				
			7.894	6.07	1300	
−15.8	36.2	36.1				
			7.747	5.88	1318	
−11.85	43.3	43.15				1327
			7.471	5.63	1327	
− 7.95	51.5	51.25				
			5.598	4.23	1323	
− 4.95	58.6	58.3				
			4.791	3.51	1365	
− 2.4	65.5	65.1				

TABLE 2.

t	P	$P(corr)$	$10^2 \Delta log\,P$	$10^5 \Delta T^{-1}$	$\dfrac{Q_1}{2.303\,R}$	mean
−21.1	28.0	27.95				
			8.828	6.66	1326	
−16.8	34.35	34.25				
			9.780	7.40	1322	
−11.85	43.05	42.9				
			11.728	8.74	1342	1344
− 5.75	56.5	56.2				
			5.132	3.81	1347	
− 3.0	63.6	63.25				
			3.304	2.39	1382	
− 1.25	68.65	68.25				

TABLE 3.

t	P	$P(corr)$	$10^2 \Delta \log P$	$10^5 \Delta T^{-1}$	$\dfrac{Q_1}{2.303\,R}$	mean
−24.6	[24.9]	24.85				
			10.160	9.27	[1096]	
−18.75	31.5	31.4				
			11.955	8.91	1342	
−12.85	41.5	41.35				1329
			11.309	8.53	1326	
− 6.95	53.9	53.65				
			9.063	6.87	1319	
− 2.0	66.5	66.1				

value of Q_1 is in accordance with this supposition; the region where compound coexists by the side of gas, lies namely on the side of higher pressure with respect to the three-phase line.

When we take the mean value from the three tables, it appears that the value for $\dfrac{Q_1}{2.303\,R}$ amounts to 1333, from which follows the value 6090 for Q_1.

The external work in the transformation amounts to RT', because one gramme-molecule of gas is formed in the conversion; at the quadruplepoint ($t = -0.4°$; see § 9) this work is 541 cal.

The change of energy amounts, therefore, to 5550 cal. The transformation is given by:

$$H_2S \cdot n\, H_2O \rightleftarrows H_2S + n\, H_2O - 5550\ cal.$$
$$(solid) \qquad\quad (gas) \qquad (solid)$$
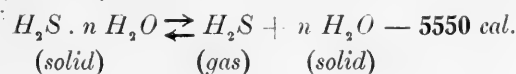
9. *The Three-Phase Line Hydrate-Aqueous Liquid-Gas.*

In the tables 4—6 the results are recorded, which were obtained with the same samples as those in § 8. In the fifth column a represents the number of volumes H_2S of one atmosphere, (corrected for $0°$), which dissolves in one volume of water. [1]) It follows from this by a simple calculation on assumption of HENRY's law that in one gramme-molecule of water $1.057.10^{-5}\, aP$ gramme-molecules of sulphuretted hydrogen dissolve; this amount is indicated by q.

In the tables b gives the absolute value of $\dfrac{(1 + r - s)\, \Delta \log P}{\Delta\, T^{-1}}$

2.303 R (see equation 13), r and s have been calculated according to 10a and b, in which the value 6 was substituted for n.

The found values of E_2 can now serve for the calculation of that value at the quadruple point.

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[1]) LANDOLT—BÖRNSTEIN —ROTH. Tables p. 601. Determinations by WINKLER.

TABLE 4.

t	P	P_{H_2O}	P_{H_2S}	a	$10^3 q$	$10^4 \frac{P_{H_2O}}{P_{H_2S}}$	$10^3 r$ (n=6)	$10^2 s$ (n=6)	rQ_v	sQ_0	$1+r-s$	$10^5 \Delta T^{-1}$	$10^2 \Delta \log P$	b	E_2	$E_2(t=-0.4)$	mean
0.85	83.5	0.5	83.0	4.497	3.945	60	5.86	2.37	63	108	0.9822	1.39	4.726	15250	14750	14660	
1.9	93.1	0.55	92.55	4.347	4.253	59	5.75	2.55	62	116	0.9803	1.32	4.135	14020	13530	13380	
2.9	102.4	0.55	101.85	4.210	4.532	54	5.25	2.72	56	124	0.9781	1.31	4.470	15240	14760	14560	14110
3.9	112.5	0.6	112.9	4.076	4.864	53	5.15	2.92	55	133	0.9760	1.23	4.295	15560	15090	14840	
4.85	125.3	0.65	124.65	3.954	5.210	52	5.04	3.13	54	143	0.9737	2.58	8.175	14070	13620	13290	
6.85	151.25	0.75	150.5	3.710	5.902	50	4.82	3.54	52	161	0.9694	2.53	8.488	14820	14390	13950	
8.85	183.9	0.85	183.05	3.485	6.743	46	4.41	4.05	47	185	0.9639						

TABLE 5.

t	P	P_{H_2O}	P_{H_2S}	a	$10^3 q$	$10^4 \frac{P_{H_2O}}{P_{H_2S}}$	$10^3 r$ (n=6)	$10^2 s$ (n=6)	rQ_v	sQ_0	$1+r-s$	$10^5 \Delta T^{-1}$	$10^2 \Delta \log P$	b	E_2	$E_2(t=-0.4)$	mean
−0.05	74.0	0.45	73.55	4.628	3.598	61	5.97	2.16	64	98	0.9844	1.34	4.722	15840	15340	[15290]	14330
+0.95	82.5	0.5	82.0	4.482	3.885	61	5.96	2.33	64	106	0.9827	2.58	8.701	15120	14630	14510	(resp.
2.9	100.8	0.55	100.25	4.210	4.461	55	5.35	2.68	57	122	0.9786	2.61	8.680	14840	14370	14140	14570)
4.9	123.1	0.65	122.45	3.948	5.110	53	5.14	3.07	55	140	0.9744	2.57	8.757	15140	14680	14350	
6.9	150.6	0.75	149.85	3.704	5.867	50	4.82	3.52	52	161	0.9696						

TABLE 6.

t	P	P_{H_2O}	P_{H_2S}	a	$10^3 q$	$10^4 \frac{P_{H_2O}}{P_{H_2S}}$	$10^3 r$ (n=6)	$10^2 s$ (n=6)	rQ_v	sQ_0	$1+r-s$	$10^5 \Delta T^{-1}$	$10^2 \Delta \log P$	b	E_2	$E_2(t=-0.4)$	mean
0.97	82.5	0.5	82.0	4.479	3.882	61	5.96	2.33	64	106	0.9827	2.68	8.959	14990	14500	14370	
3.00	101.4	0.55	100.85	4.196	4.473	55	5.35	2.68	57	122	0.9786	2.65	8.913	15010	14540	14310	14370
5.03	124.5	0.65	123.85	3.931	5.146	52	5.04	3.09	54	141	0.9741	2.59	8.867	15210	14760	14420	
7.05	152.7	0.75	151.95	3.686	5.920	49	4.73	3.55	51	162	0.9692						

The situation of the quadruple point could be found by graphically determining the point of intersection of the two three-phase lines SS_BG and SL_2G. In this way by the aid of the data recorded in the tables 1—6 we find $t = -0.6 \pm 0.2$; the corresponding pressure amounts to about 70 cm. of mercury. The quadruple point temperature can, however, be calculated more accurately as follows.

Under the circumstances of the quadruple point the liquid L_2 is a diluted solution of sulphuretted hydrogen in water. When a again represents the number of volumes H_2S of one atmosphere (corrected for $0°$), which dissolves in one volume of water, the number of gramme-molecules H_2S that dissolves in 100 grammes of water, is $5.87 . 10^{-5} aP$. If H_2S were a non-electrolyte, the lowering of the freezing-point would accordingly amount to $5.87 . 10^{-5} aP . 18.5°$. When in this we introduce for a and P the solubility at $t = -0.6°$ (4.709) and the quadruple point pressure found graphically (70), we find a lowering of the freezing point of $0.4°$; the quadruple point temperature amounts, therefore, to $-0.4°$ C. When for a the solubility at $-0.4°$ is chosen, this brings no change in the calculation.

Nor does the fact that sulphuretted hydrogen in water is partially electrolytically dissociated bring a change in the above calculation. The dissociation constant of H_2S amounts (first stage) to about 10^{-7}. The dilution under the circumstances of the four-phase equilibrium amounts to 5.2, the degree of dissociation in consequence of this to about 7.10^{-4}, and consequently the latter has no appreciable influence on the situation of the quadruple point.

In order to find the value of E_2 at this temperature, the specific heats of the reacting substances must be known. As the molecular specific heat of the hydrate ($n = 6$) would amount to 61.6 according to the law of Kopp [1]), and as the specific heat of six molecules of water and one mol. of sulphuretted hydrogen is $108 + 6.3 = 114.3$, the algebraic sum is about 53. The correction required for the calculation of E_2 at the quadruple point is, therefore, $53 (t + 0.4)$. The mean of the values thus found is recorded in the last column of the tables 4—6.

The values of the last column but one in tables 4 and 5 still present appreciable deviations. This is owing to the small differences of temperature between the successive observations. In order to determine these differences more accurately the Anschütz-thermometer (division into $1/5$ degree), which was used in the other determinations, was replaced by a Beckmann-thermometer (division

[1]) Nernst. Theoretische Chemie. Gesetz von Dulong und Petit.

into $^1/_{50}$ degree) in the experiments of table 6. Consequently the agreement of the values in the last column but one of table 6 is much better; the mean values of the three tables are in good concordance.

When we now determine the mean of the values from the last columns of tables 4—6, the first value of table 5, which is evidently too high (probably because the transformation in the quadruple point had not yet entirely taken place), being eliminated, the value 14270 for E_2 is found; when the value in question *is* taken into account, the mean amounts to 14350 cal.

Hence the decomposition of the hydrate takes place according to:

$$H_2S \cdot n\, H_2O \rightleftarrows H_2S + n\, H_2O - 14270\ (14350)\ cal.$$
$$(solid) \qquad (gas) \quad (liquid)$$
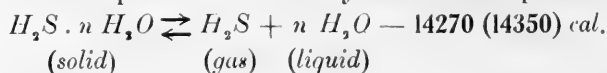
An objection that may be adduced against the above calculations, is the choice of $n = 6$ in the determination of r and s from equation 10 a and b, and in the calculation of the algebraic sum of the specific heats. We shall come back to this in § 11.

10. From the values $E_1 = 5550$ cal. (§ 8) and $E_2 = 14270$ (14350) cal. (§ 9) follows according to equation $1 : n\, Q = 8720$ (8800) cal., and as $Q = 1440$ cal., the value 6.06 (6.11) follows for n. Hence the conclusion from these calculations is, that the hydrate has the formula:

$$H_2S \cdot 6\ H_2O.$$

11. As was stated in § 9, $n = 6$ was already taken in the calculation. A choice of n was necessary to render it possible to calculate r and s (equation 10. a and b), and find the algebraic sum of the specific heats. We shall, therefore, still have to show that $n = 6$ is the only value that satisfies the observations. It might, namely, also be possible that with the choice $n = 5$ the result of § 10 was also appreciably changed, and would correspond to the choice $n = 5$. This is, however, not the case. The following considerations may make this clear.

If $n = 5$, the molecular specific heat of the hydrate would amount to 53.0, and as the specific heat of five molecules of water and one mol. of sulphuretted hydrogen is $90 + 6.3 = 96.3$, the algebraic sum would be about 43.

When on assumption $n = 5$ we calculate the values of r and s, and by the aid of this the other values, it appears that this does not give any change in the result, and that, therefore, the assumption $n = 5$ is erroneous. We have carried out this calculation for the data of table 4; the results are recorded in table 4a. The mean

value of the last column becomes 100 cal. higher than the corresponding value of table 4. A difference of one molecule of water

TABLE 4a.

t	$\dfrac{10^3 r}{(n=5)}$	$\dfrac{10^2 s}{(n=5)}$	rQ_v	sQ_0	$1+r-s$	b	E_2	$E_2(t=-0.4)$	mean.
0.85	5.88	1.97	63	90	0.9862				
						15310	14800	14720	
1.9	5.78	2.13	62	97	0.9845				
						14080	13570	13450	
2.9	5.28	2.27	57	104	0.9826				
						15310	14810	14650	
3.9	5.17	2.43	56	111	0.9809				14210
						15640	15150	14940	
4.85	5.06	2.61	54	119	0.9790				
						14150	13670	13400	
6.85	4.85	2.95	52	135	0.9754				
						14920	14460	14110	
8.85	4.44	3.37	47	154	0.9707				

in the composition of the hydrate would require a difference of 1440 cal., and besides the difference lies in the wrong direction. Accordingly the value $n = 5$ does not correspond to the observations.

It will be clear from the tables 4—6 that it is permissible to neglect the values spoken about in § 6 in the expressions 10a and b.

12. When we now compare the results of this indirect analysis with the determinations carried out before by a direct way, it appears that at the quadruple point the composition of the compound is given by $H_2S . 6H_2O$, that, however, at —80°, when the compound is formed of water and an excess of sulphuretted hydrogen, a quantum of gas is persistently retained by the solid substance, which does not even escape at a pressure of 2 cm. (waterjet pump) in some hours. When the compound is heated, this gas is, however, quickly liberated, and this latter causes two-phase equilibria to be measured in vapour pressure determinations at low temperatures (Cf. § 7).

The analyses executed before can be explained by this gas-adsorption. The quantity of sulphuretted hydrogen retained was not inconsiderable. When we bear in mind that the composition of the solid substance varied between $H_2S . 5.1H_2O$ and $H_2S . 5.5H_2O$, it appears that per molecule $H_2S . 6H_2O$ resp. 0.18 and 0.09 mol. H_2S have remained adsorbed. That these quantities have not rendered the above three-phase determinations impossible is owing to this that during the filling of the apparatus, it was repeatedly evacuated cooled with liquid air, hence at lower pressure, that therefore the sulphuretted hydrogen could more easily escape, and the time of evacuation was chosen long.

In the direct analysis exhaustion with liquid air is not permissible,

because the pressure then falls below the three-phase tension SS_BG, in other words the hydrate can be decomposed. From the determinations of the tables 1—3 the three-phase pressure hydrate-ice-gas at —80° can be calculated by extrapolation. When we assume the heat of transformation to be independent of the temperature — it has already been proved in § 5 that the influence of the temperature is small — the following equation is found for the three-phase line SS_BG by the aid of the tables 1—3:

$$log\ P = -\frac{1333}{T} + 6,7393.$$

When in this we substitute $t = -80°$ C., the pressure appears to amount to 7 mm. In the carbonic acid-alcohol mixture the three-phase tension may certainly not be neglected. In the filling of the apparatus in the evacuation with cocoanut carbon we have, therefore, to do both with slowly decreasing adsorption, and with decomposition of the hydrate. It appears from the above-described observations that the time of evacuation can easily be chosen so that neither has a disturbing influence in the determination of the equilibrium pressures.

Decomposition of the hydrate should, however, be avoided in the direct analysis. The pressure of the waterjet pump lies sufficiently high above the three-phase pressure, that decomposition may be left out of account; under these circumstances the adsorption can, however, not be abolished in a few hours. Improvement in the direct analysis method is only possible by choosing the time of evacuation longer. We have still performed three direct analyses in the way described above (cf. § 1 loc. cit.), in which the time during which the hydrate remained connected with the waterjet pump, was carried up to 5 (one determination) resp. 7 (two determinations) hours. Notwithstanding this these determinations yielded for the water content 5.39, 5.46, and 5.61 H_2O. Only the last value falls somewhat outside the limits 5.1 to 5.5 of the determinations performed before (see § 1). Accordingly the value 6 is far from being reached here either.

The gas-adsorption discussed here is, therefore, the cause that the sulphuretted hydrogen hydrate has not yet been prepared by a direct way in pure state, and that it cannot be analysed either, but that an indirect method which can be applied here at temperatures where this adsorption is no longer active, yields the right composition for this substance. At these temperatures direct analysis is, however, impossible on account of the great tension of dissociation.

Delft—Amsterdam, March 22, 1919.

Chemistry. — *"On the Phenomenon of Anodic Polarisation."* II.
By Prof. A SMITS. (Communicated by Prof. P. ZEEMAN).

(Communicated in the meeting of March 29, 1919).

1. In this communication will be discussed the peculiar pheno-
menon that was mentioned in the first communication with the above
title. As was already stated there I observed the described pheno-
menon for the first time with Mr. LOBRY DE BRUYN for iron and
nickel more than two years ago, but I did not publish it, because
I thought it necessary to study the phenomenon first more closely.

Afterwards the same phenomenon was found by Mr. ATEN [1]) for
chromium, but most probably he has not interpreted it correctly.

Explanation of the Phenomenon.

2. It has appeared from the preceding communication that the
"phenomenon" appeared for iron when this was polarized anodically
in a solution of ferro-sulphate or ferro-chloride, which had, indeed,
been freshly prepared, but had not beforehand been heated with
iron-powder.

We have already pointed out before that iron in the state of
internal equilibrium can only coexist with a solution which practi-
cally possessed no ferri-ions. It is further known that a solution in
which ferri-ions occur, clearly disturbs iron, and the more strongly
as the ferri-ion-concentration is greater. As we communicated already
before we have even succeeded in making iron passive by simply
immersing it in a concentrated solution of ferri-nitrate.

Hence the potential of the iron is less negative in a solution that
contains ferri-ions than in a solution that coexists with unary iron,
which latter solution is practically free from ferri-ions. In the solution
with which the "phenomenon" was obtained the iron accordingly
did not present the potential of internal equilibrium, but the potential
was less negative.

When now iron in such a liquid is anodically brought to solution,
the electrolyte will undergo a change in the neighbourhood of the
iron, because iron when it is not passive, certainly goes into solution
practically exclusively as ferro-ion. The iron is disturbed during this
anodic dissolving, as appears from the less negative potential of the
iron during the passage of the current, and at the same time the
iron gets surrounded by a liquid layer that is poorer in ferri-ions

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[1]) These Proc. XX, p. 1121.

than the other part of the solutions. After the current has been broken the iron surface is transformed with pretty great velocity in the direction of the internal equilibrium, and as it is surrounded by a solution that contains fewer ferri-ions than the solution outside the boundary layer, the potential of the iron will now be more negative than before the anodic polarisation. This state can, however, last only a very short time, for the ferri-ions diffuse from outside into the boundary layer, in consequence of which the potential must again become less negative, and will rise to the original value.

For a right understanding of the matter it is useful to study the subjoined diagram.
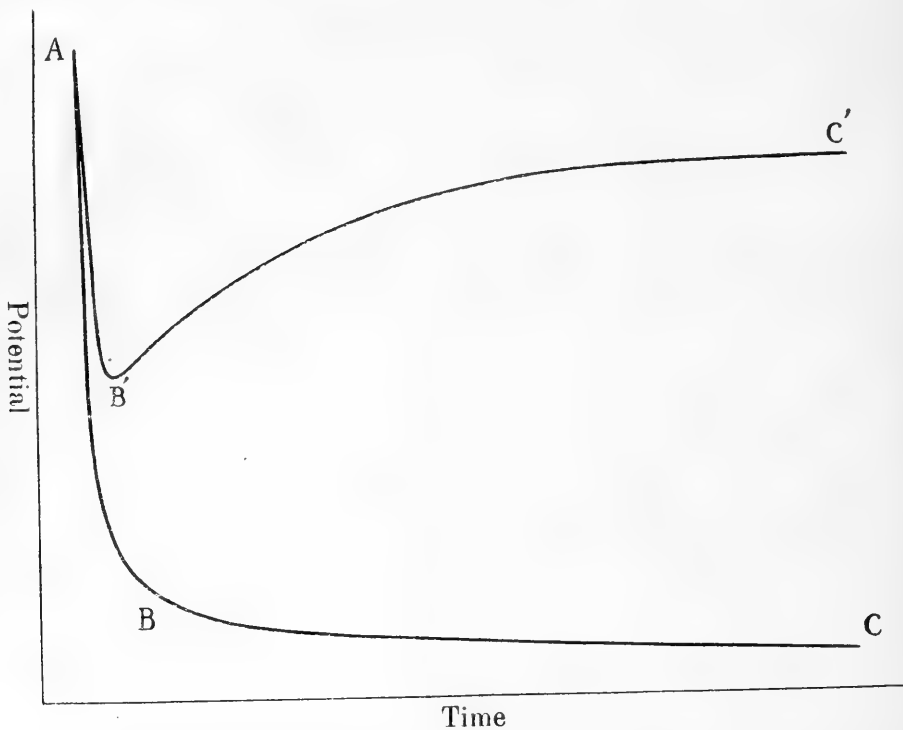
The line ABC represents the course of the potential of iron after anodic polarisation, when it is immersed in the solution of a ferro-salt, which is practically free from ferri-ions. Immediately after the anodic polarisation the iron is pretty greatly disturbed, but this disturbance diminished at first with great velocity, and afterwards more slowly. The curve $AB'C''$ also indicates the course of the potential of iron after anodic polarisation, but now after a small quantity of a ferri-salt has been added to the preceding solution. At first the potential descends rapidly, to below the final value. If the liquid in the boundary layer had been entirely free from ferri-

ions and if it had remained so, the potential would have followed the curve ABC, but now the iron is, indeed, in a liquid layer that is poorer in ferri-ions than the liquid outside the boundary layer, but the ferri-ons present prevent the iron from assuming internal equilibrium, hence the potential cannot reach such a great negative value as when the ferri-ions were present, as in the first experiment.

Besides continually more ferri-ions diffuse into the boundary layer, which causes the disturbance of the iron to increase again and in consequence of which the potential becomes again less negative. When we imagine fig. 10 placed under fig. 2 of the former publication, we get the schematic figure indicated just now.

In this way the phenomenon for iron must be explained, and very probably it will have to be explained in the same way for nickel and chromium.

That for iron the minimum appears sooner and is more pronounced, must be attributed to the great rapidity with which iron, so long as it is not yet passive, tries to re-establish equilibrium after a disturbance. Nickel is much more inert in a $NiSO_4$-solution than in a $NiCl_2$-solution, and this shows itself also again in this phenomenon [1].

3. When it now appears on continued research, as is to be expected, that the discussed phenomenon can also be made to disappear for nickel and chromium by beforehand heating the electrolytes with the metals in the form of powder for a long time in a current of hydrogen, then it is sure that the solutions of nickel sulphate and chromo-sulphate used up to now contain a second kind of ions, and this in a concentration different from that prevailing in the liquid that coexists with the metal which is in internal equilibrium.

For nickel we are then confronted by the interesting question what is the second nickel-ion here.

Thus it will probably appear that the found phenomenon furnishes an excellent expedient to decide whether a solution contains different kinds of ions of a same element or whether it does not.

In conclusion I will point out that it is very well possible that as it were the reflected image of the found phenomenon can present itself after cathodic polarisation; this has, however, not been found by us as yet. The results published by RAHTERT would prove this possibility for nickel, but in our opinion these results are not correct.

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of the University.

Amsterdam, March 27, 1919.

[1] This will clearly appear in a following communication.

Mathematics. — *"Aufzählung der periodischen Transformationen des Torus"*. By Prof. L. E. J. Brouwer.

§ 1. *Transformationen mit invarianter Indikatrix und invarianter Zyklosis.*

Wir werden sagen, dass eine Transformation *die Zyklosis invariant lässt*, wenn sie *jeden Zykel* (d. h. jede nicht zusammenziehbare einfache geschlossene Kurve) *inklusive des Umlaufssinnes äquivalent transformiert.* Alsdann kann eine *n*-periodische Transformation *t* mit invarianter Indikatrix und invarianter Zyklosis des Torus *R* keinen Punkt invariant lassen[1]), so dass ihre Modulfläche[2]) nach der Hurwitz-schen Formel[3]) ein Torus *T* sein muss. Die Flächen *R* und *T* besitzen eine gemeinsame einfach zusammenhängende Ueberlagerungsfläche *S*, welche sich in solcher Weise topologisch (d. h. eineindeutig und stetig) auf eine Cartesische Ebene *C* abbilden lässt, dass die Translation von *C*

$$(\tau) \quad \ldots \quad \begin{cases} x' = x + a \ (a \text{ ganz}) \\ y' = y \end{cases}$$

der Transformation *t* und die von den Translationen

$$\begin{cases} x' = x + 1 \\ y' = y \end{cases} \quad \text{und} \quad \begin{cases} x' = x \\ y' = y + 1 \end{cases}$$

erzeugte Gruppe derjenigen Gruppe von *S*, welche alle Punkte von *T* invariant lässt, entspricht. Zwei Punkte P_1 und P_2 von *C* entsprechen nun dann und nur dann demselben Punkte von *T*, wenn sie *entweder* demselben Punkte von *R* entsprechen, *oder* P_1 durch eine Potenz von τ in einen Punkt P_3, der demselben Punkte von *R* entspricht wie P_2, übergeführt wird. Hieraus folgt *erstens*, dass eine Translation von *C* der Form

$$\begin{cases} x' = x + b \ (b \text{ ganz}) \\ y' = y + 1 \end{cases}$$

angegeben werden kann, welche alle Punkte von *R* invariant lässt,

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[1]) Diese Proceedings XXI, S. 707—710.
[2]) Ibid., S. 1143.
[3]) Math. Annalen 41, S. 404.

zweitens, dass, wenn n der Minimalwert ist, für den die Translation von C

$$\begin{cases} x' = x + n \\ y' = y \end{cases}$$

alle Punkte von R invariant lässt, die Zahlen a und n relativ prim sind. Für ein geeignetes torisches Koordinatensystem auf R wird somit die Transformation t durch folgende Formeln dargestellt:

$$\begin{cases} \varphi' = \varphi \\ \psi' = \psi + \dfrac{2\pi a}{n} \end{cases} \quad (a \text{ und } n \text{ ganz und relativ prim}).$$

§ 2. *Transformationen mit invarianter Indikatrix und variabler Zyklosis.*

Sei t die betrachtete n-periodische Transformation des Torus R, t' eine mit t korrespondierende Transformation der einfach zusammenhängenden Ueberlagerungsfläche S von R. Alsdann geht t' durch eine geeignete topologische Abbildung von S auf eine Cartesische Ebene C in eine Transformation t'' von C über, welche von einer periodischen, ganzzahligen, homogen-linearen Transformation der Determinante $+1$ nur beschränkte Abweichungen aufweist, mithin sich, ebenso wie die letztere Transformation, periodisch, eineindeutig und stetig auf den unendlichfernen Kreis von C ausdehnen lässt, wobei dieser Kreis einen invarianten Umlaufssinn, mithin keinen invarianten Punkt besitzt, so dass t'' im endlichen von C und deshalb auch t auf R einen invarianten Punkt besitzen muss. Weil somit die Modulfläche B von t von R *nicht* unverzweigt überdeckt wird, so bezizt B nach der obigen HURWITZschen Formel den Zusammenhang der Kugel und liegt R nach der Art einer regulären Riemannschen Fläche vom Geslecht 1 n-blättrig und mit einem n-blättrigen Verzweigungspunkte im eben ermittelten für t invarianten Punkte über B ausgebreitet. Hieraus folgt, dass nur vier Fälle möglich sind [1]:

I. $n = 2$; R überdeckt B mit vier zweiblättrigen Verzweigungspunkten.

II. $n = 6$; R überdeckt B mit einem zweiblättrigen, einem dreiblättrigen und einem sechsblättrigen Verzweigungspunkt.

III. $n = 4$; R überdeckt B mit zwei vierblättrigen und einem zweiblättrigen Verzweigungspunkt.

IV. $n = 3$; R überdeckt B mit drei dreiblättrigen Verzweigungspunkten.

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[1] APPELL et GOURSAT, *Théorie des fonctions algébriques*, Paris, Gauthier-Villars, 1895, S. 241.

In jedem dieser vier Fälle ist die Transformation t durch die angegebene Struktur der entsprechenden Riemannschen Fläche vollständig charakterisiert.

§ 3. *Involutorische Transformationen mit umkehrender Indikatrix.*

Wir bezeichnen die Menge der für die betrachtete Transformation t des Torus R invarianten Punkte mit I. Alsdann sind drei Fälle zu unterscheiden:

α. Die Komplementärmenge von I in R besteht aus mehr als einem Gebiete. Weil keines dieser Gebiete von t in sich mit invarianten Randpunkten transformiert werden kann, so werden dieselben von t paarweise verwechselt. Zwei derartige von t verwechselte Gebiete g_1 und g_2 müssen aber eine gemeinsame Grenze besitzen, welche sowohl für g_1 wie für g_2 unbewallt[1]) ist, was nur möglich ist, wenn sie aus zwei äquivalenten Zykeln besteht. Dann aber wird t für ein geeignetes torisches Koordinatensystem wie folgt dargestellt:

$$\begin{cases} \varphi' = -\varphi \\ \psi' = \psi. \end{cases}$$

β. Die Komplementärmenge von I in R besteht aus einem einzigen, nicht mit R identischen Gebiete g. Wenn g nicht schlichtartig wäre, so würde mit t eine involutorische Transformation mit umkehrender Indikatrix der einfach zusammenhängenden Ueberlagerungsfläche S von R, deren invariante Punkte nur ein einziges Gebiet begrenzten, korrespondieren, was unmöglich ist. Weil mithin g schlichtartig ist, so werden seine Ränder von t paarweise verwechselt[2]). Zwei derartige von t verwechselte Ränder r_1 und r_2 sind aber beide für g unbewallt, so dass sie in einem Zykel k von R zusammenfallen und das Gebiet $g + k$ nicht mehr schlichtartig ist. Eventuelle Ränder des Gebietes $g + k$ müssten einerseits für t invariant sein, andererseits von t paarweise verwechselt werden, können mithin nicht existieren, so dass $g + k$ mit R identisch ist und t für ein geeignetes torisches Koordinatensystem wie folgt dargestellt wird:

$$\begin{cases} \varphi' = -\varphi \\ \psi' = \psi + \varphi. \end{cases}$$

γ. Die Menge I fällt fort. In diesem Falle besitzt t eine geschlossene, einseitige Modulfläche M, welche R als ihre zweiseitige Verdoppelung besitzt, mithin notwendig eine einseitige Ringfläche sein muss. Wir können also auf M zwei einander nicht treffende einseitige Zykeln r_1 und r_2 wählen. Weil r_1 und r_2 die nicht zu ihnen gehörenden

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[1]) Math. Annalen 71, S. 321.

[2]) Ibid. 80, S. 36—41.

Punkte von M nicht in getrennte Gebiete zerlegen, so können auch die Bilder s_1 und s_2 auf R von r_1 und r_2 die nicht zu ihnen gehörenden Paare von für t äquivalenten Punkten von R nicht in getrennte Gebiete zerlegen, d. h. s_1 und s_2 zerlegen R in zwei für t äquivalente Gebiete und t wird für ein geeignetes torisches Koordinatensystem wie folgt dargestellt:

$$\begin{cases} \varphi' = -\varphi \\ \psi' = \psi + \pi. \end{cases}$$

§ 4. *Nicht-involutorische Transformationen mit umkehrender Indikatrix.*

Sei t die betrachtete $2n$-periodische Transformation des Torus R. Weil für $n > 1$ keine $2n$-periodische, ganzzahlige, homogen-lineare Transformation der Determinante -1 in zwei Variabeln existiert, so lässt t^2 die Zyklosis von R invariant, besitzt mithin als Modulfläche einen Torus T, auf welchem das Bild von t eine involutorische Transformation t_1 mit umkehrender Indikatrix darstellt. Wir führen auf T die nach § 3 zu t_1 gehörigen torischen Koordinaten φ und ψ ein, betrachten zwei durch die Gleichungen $\varphi = a$ und $\varphi = -a$ bestimmte Zykeln r_1 und r_2 von T und bezeichnen die Bildzykeln von r_v auf R mit $_1 s_v, {}_2 s_v, \ldots {}_m s_v$. Weil alle Zykeln $_v s_v$ für t äquivalent sind und ihre zyklische Reihenfolge von t umgekehrt wird, so kann ihre Anzahl nur *zwei* betragen und muss $m = 1$ sein. Mithin wird die alle Punkte von R invariant lassende Transformationsgruppe der einfach zusammenhängenden Ueberlagerungsfläche S von R und T durch die Translationen

$$\begin{cases} \varphi' = \varphi \\ \psi' = \psi + 2n\,\pi \end{cases} \quad \text{und} \quad \begin{cases} \varphi' = \varphi + 2\pi \\ \psi' = \psi + 2h\,\pi \end{cases}$$

erzeugt. Wenn wir nunmehr φ und $\psi - h\varphi$ auf T als neue torische Koordinaten (φ, ψ) einführen, so werden diese Translationen durch

$$\begin{cases} \varphi' = \varphi \\ \psi' = \psi + 2n\,\pi \end{cases} \quad \text{und} \quad \begin{cases} \varphi' = \varphi + 2\pi \\ \psi' = \psi \end{cases}$$

und t_1 durch

$$\begin{cases} \varphi' = -\varphi \\ \psi' = \psi + k\varphi \end{cases} \quad \text{bzw.} \quad \begin{cases} \varphi' = -\varphi \\ \psi' = \psi + k\varphi + \pi, \end{cases}$$

mithin t in denselben Koordinaten durch

$$\begin{cases} \varphi' = -\varphi \\ \psi' = \psi + k\varphi + 2q\pi \end{cases} \quad \text{bzw.} \quad \begin{cases} \varphi' = -\varphi \\ \psi' = \psi + k\varphi + (2q+1)\,\pi, \end{cases}$$

also auf jeden Fall durch

$$\begin{cases} \varphi' = -q \\ \psi' = \psi + k\,\varphi + g\,\pi \end{cases}$$

und in korrespondierenden torischen Koordinaten *von* R durch

$$\begin{cases} \varphi' = -\varphi \\ \psi' = \psi + \dfrac{k}{n}\,\varphi + \dfrac{g}{n}\,\pi \end{cases}$$

dargestellt. Auf Grund der Eindeutigkeit von t auf R muss $\dfrac{k}{n} =$ einer ganzen Zahl e sein. Indem wir aber für geeignetes b, φ und $\psi - b\varphi$ auf R als neue torische Koordinaten (φ, ψ) einführen, können wir erreichen, dass e entweder $= 0$ oder $= 1$ wird, so dass wir schliesslich für t zu den folgenden Formeln gelangt sind:

$$\begin{cases} \varphi' = -\varphi \\ \psi' = \psi + \dfrac{g}{n}\,\pi \end{cases} \quad \text{bzw.} \quad \begin{cases} \varphi' = -q \\ \psi' = \psi + \varphi + \dfrac{g}{n}\,\pi \end{cases}$$

wo g und n relativ prim sind.

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