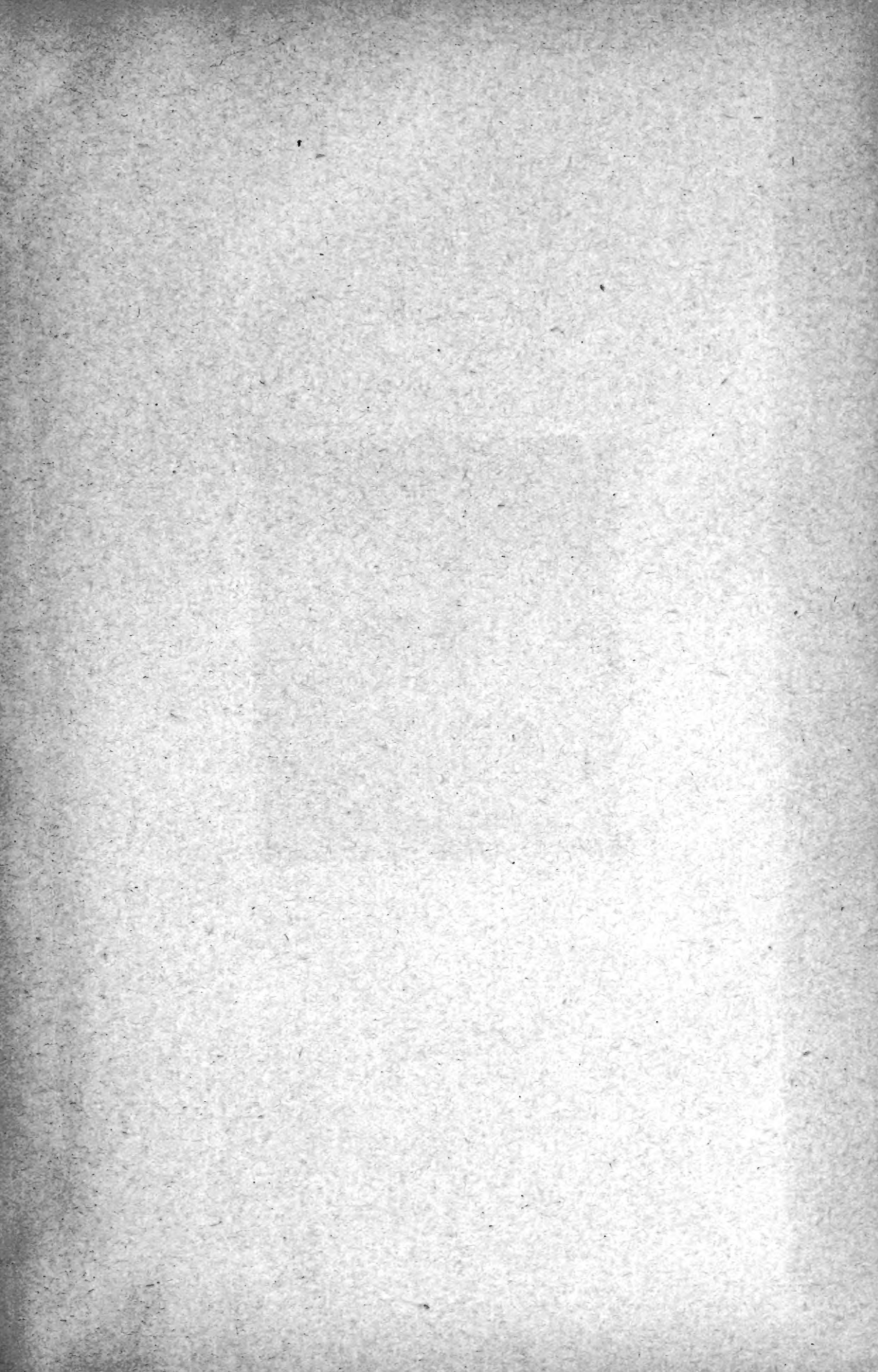
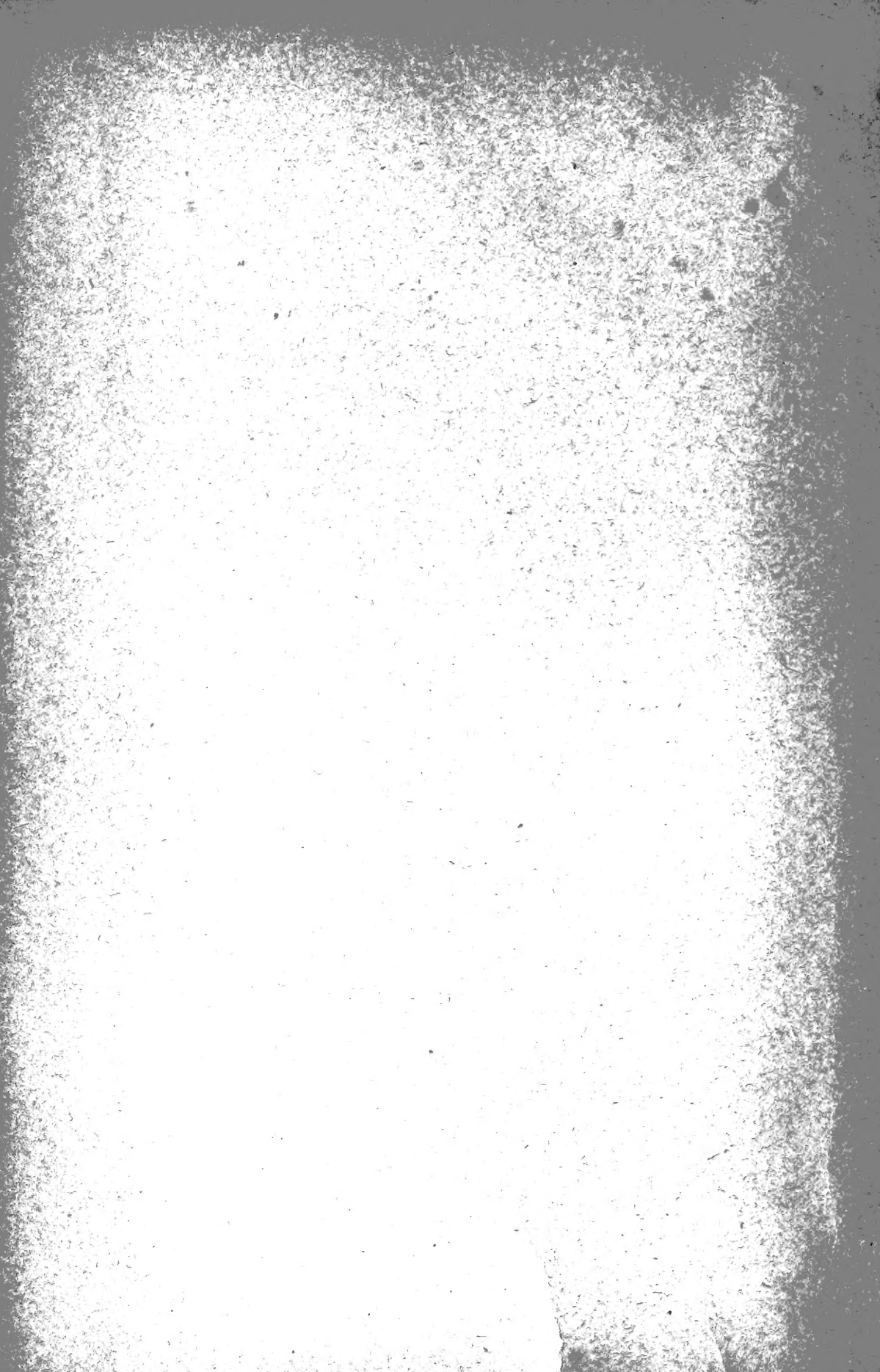


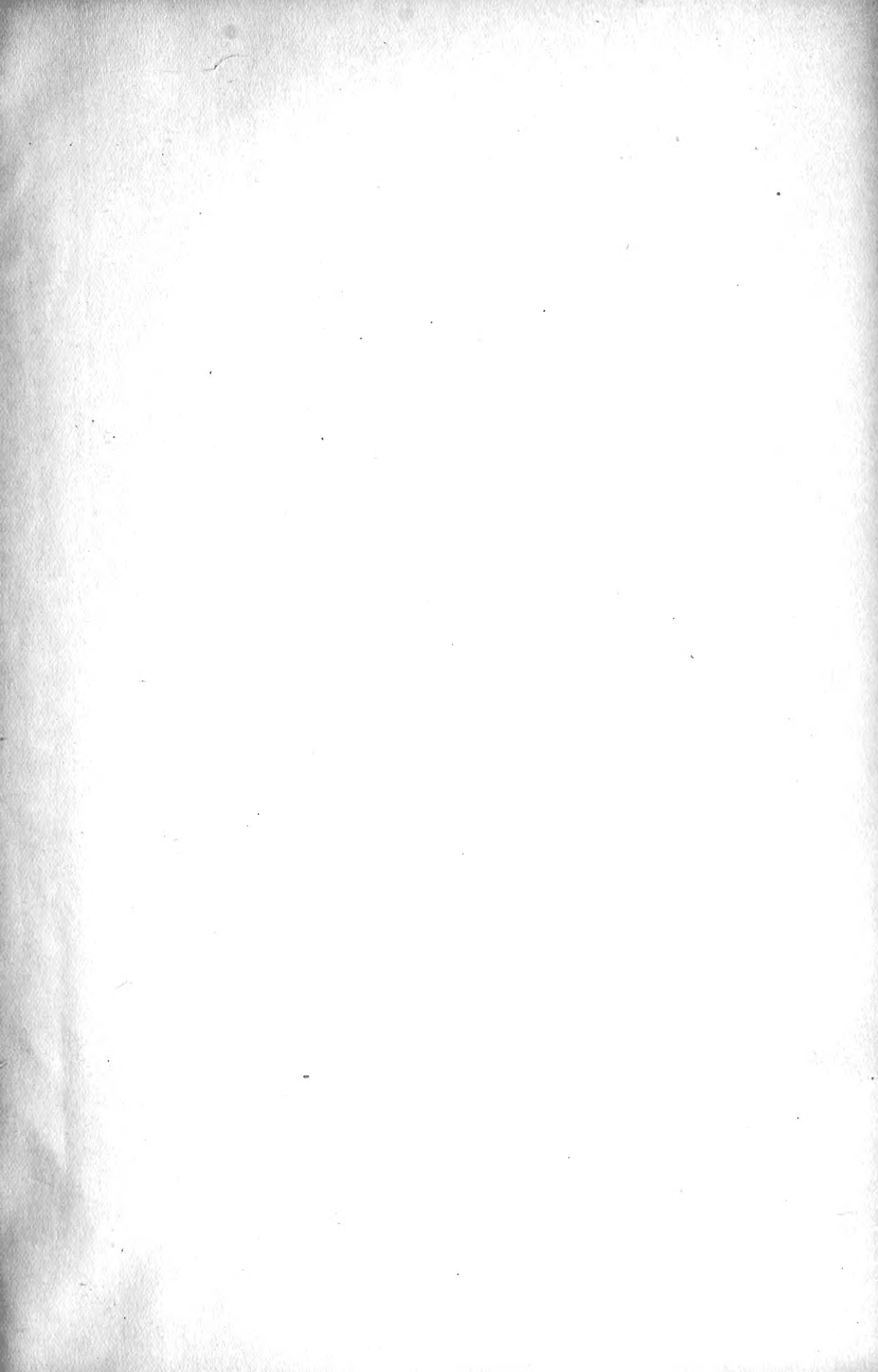
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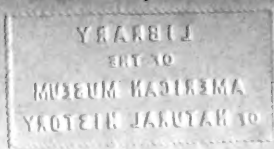
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SECTION OF SCIENCES

VOLUME XI

JOHANNES MÜLLER :-: AMSTERDAM
:=====: JULY 1909 :=====:



(Translated from: Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige
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09-41077-160027

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETINGS
of Saturday May 30 and June 27, 1908.

(Translated from: Verslag van de gewone vergaderingen der Wis- en Natuurkundige
Afdeling van Zaterdag 30 Mei en Zaterdag 27 Juni 1908, Dl. XVII).

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By A. P. H. TRIVELLI. (Communicated by Prof. S. HOOGWERFF).

(Communicated in the Meeting of March 28, 1908).

I. *The image.*

In order to enquire into the density gradation a photographic plate may be exposed in two ways:

- a. with constant light intensity and varying time of exposure;
- b. by equal exposures, with different light intensities.

In order to eliminate the possibility of other circumstances being different, particularly those under which development is carried out, the first method has been adopted, a plate being divided into strips, and each succeeding strip receiving a longer exposure than the preceding one. This is combining several trial plates into one. In my opinion an “image” cannot be said to appear in this case; it only appears if the second method is adopted.

The results obtained by equal exposures with different light intensities I will call *copies*. A copy always shows an image, which may be positive or negative.

By a *normal* or non-polarized copy I understand copying positive-negative-positive- etc., which may be represented by

$$\pm \rightarrow \mp$$

By a *polarized* copy I understand copying positive-positive-etc. or negative-negative- etc., which may be represented by

$$\pm \rightarrow \pm$$

According to the investigations of WARNERKE¹⁾, W. ABNEY²⁾, K. SCHAUM and V. BELLACH³⁾, R. NEUHAUS⁴⁾, and W. SCHEFFER⁵⁾, the differences in density which appear in a photographic plate after exposure and development, may be ascribed to differences in the depth of the reduced silver haloid. So the image must have a

¹⁾ Phot. Archiv. 1881; S. 85 u. 119.

Phot. Mitt. Bd. 18; S. 65, 98 u. 235.

J. M. EDER, Handb. d. Phot. 1902; Bd. III; S. 106 u. 108.

²⁾ J. M. EDER, Hand. d. Phot. 1902; Bd. III; S. 102.

³⁾ Phys. Zeitsch. 1902; Bd. IV; S. 4.

J. M. EDER, Handb. d. Phot. 1903; Bd. III; S. 819.

⁴⁾ Wied. Annal. d. Phys. u. Chem. 1898; Bd. 65; S. 164.

⁵⁾ Phot. Chronik. 1904; S. 366.

Phot. Rundschau. 1904; S. 121.

plastic shape similar to that formed by the pigment-gelatine printing process, the insoluble part being a normal copy, the soluble part a polarized one (monochrome pinatypy).

It is characteristic of the normal copy, if exposed and developed normally that the portions where the density is greatest show a duller surface when seen by light reflected at an angle than the clearest portions. This is to be attributed to the presence of reduced silver-haloid grains immediately under the free surface.

If the image lies against the free surface, it may be called a surface image, in opposition to a "depth" image, with which this is not the case.

The cause of the appearance of the surface image has been ascribed by P. H. EYKMAN and myself¹⁾ to the surface tension of the wet gelatine. So a silver-haloid gelatine layer may be looked upon as consisting of a series of layers, of which the top one, i.e. the one at the free surface, is the most sensitive, while every succeeding one lying under it, is less sensitive. The exposure required to render a beginning of reduction by the developer visible, the liminal value ("Schwellenwert") consequently seems to increase in proportion to the depth; that of the topmost layer is equal to the liminal value of the plate itself. We will call this the "absolute", that of the succeeding layers the "relative" liminal value.

Leaving aside, for clearness's sake, the mutual differences in sensitiveness of silver-haloid grains in one single layer, to which J. M. EDER²⁾ and J. PLENER³⁾ have drawn attention, the differences in size and shape and the topographic situation of the grains, the normal copy may be represented as is shown in cross section and graphically in fig. 1.

The shape of the image of a polarized copy might be represented as indicated in fig. 2. I have found that this explanation cannot be applied to a single photographic image, but it is applicable to chemigraphic processes, catatypy and the silver-pigmentgum process.

In the case of some polarized copies, as the counter-positive and -negative, a normal copy is developed first, the reduced silver haloid of which is dissolved and, after a diffused exposure, redeveloped. Now a depth image originates (fig. 3). Owing to the diffused exposure the base of it, leaving aside slight differences in light absorption, will everywhere be about equally distant from the free surface.

¹⁾ Drude. *Annal. d. Phys.* 1907; Bd. 22; S. 119.

²⁾ J. M. EDER, *Handb. d. Phot.* 1902; Bd. III; S. 64.
Phot. News. 1883; p. 81.

³⁾ *Phot. Korresp.* 1882; S. 306.

According to the investigations of E. ENGLISH¹⁾ and J. M. EDER²⁾ there are two images in the case of solarization. This question has not yet been satisfactorily cleared up, and a certain amount of confusion prevails as to the distribution of the normal and the polarized copy.

If the time of exposure, resp. the light intensity is increased, the reducibility of the silver haloid increases in depth, finally to such a degree that provided the time of development be sufficient, the reduction extends to the glass, as is shown by the excellent microscopic preparations of W. SCHEFFER³⁾. If solarization sets in, it will first occur in the apparently most sensitive layers, i. e. those at the free surface; consequently the reducibility decreases from there, and on the time of exposure, resp. the intensity of the light being increased, it constantly extends further down. Thus an image is obtained as is graphically shown by fig. 4, from which it is at once apparent *that the solarized image is a normal copy and a surface image*. Under this image there is a polarized copy of greater density with *AB* for its base and from there to the glass there is a strip of fog, the density of which depends on the thickness of the emulsion.

That after all, in the case of solarization, the copy appears polarized, is therefore owing to the normal copy being of less density than the polarized one. It will, however, more or less reduce the contrasts and the wealth of detail. *It is consequently contrary to fact to understand polarization by solarization, as is always done.*

(In the figure the section of the solarized image is indicated by finer granulation, which is meant to show that the density has been reduced in that portion).

This at once accounts for the phenomenon occurring in the case of solarization of silver iodide gelatine discovered by LÜPPO-CRAMER⁴⁾

1) Phys. Zeitschr. 1900; Bd. 2; S. 62.

J. M. EDER, Jahrb. f. Phot. u. Repr. 1902; S. 79.
Archiv. f. wiss. Phot. 1900; Bd. II; S. 260.

2) Zeitschr. f. wiss. Phot. 1905; Bd. II; S. 340.

J. M. EDER, Handb. d. Phot. 1906; Bd. I; T. 2; S. 287.

Sitzungsber. d. Kaiserl. Akad. d. Wiss. zu Wien. Mathem-Naturw. Klasse; Bd. CXIV; Abt. IIa; Juli 1905.

3) J. M. EDER, Jahrb. f. Phot. u. Repr. 1907; S. 31.

4) I cannot omit quoting this experiment, which so clearly confirms the above:
"Eine auffallende Erscheinung beobachtete ich endlich noch bei einem *Solarisierungsversuch* mit Jodsilbergelatine. Unter einem Negativ ergaben die Platten in "drei Sekunden bei diffussem Tageslicht ein ausexponiertes Bild. Eine sechs Stunden "lang unter demselben Negativ belichtete Platte schien sich in Amidolpottasche, "in welcher sie neben der drei Sekunden belichteten Platte entwickelt wurde, zuerst

and which points to the very rapid decrease in reducibleness of silver iodide when solarized.

II. *A few phenomena occurring with solarization accounted for by considering the form of the image.*

From the form of the image in fig. 4 it appears how impregnation of the silver-haloid gelatine plate with bichromate before exposure may influence the result obtained, which was pointed out by BOLAS¹⁾. J. M. EDER and G. PIZZIGHELLI²⁾ attributed the result exclusively to hardening of the gelatine, by which development in the normal image is disturbed, and in which solarization acts hardly any part. It is evident that this image in the hardened gelatine more or less coalesced with the solarized image, in proportion to the strength of the bichromate solution employed, by which the development of the latter is suppressed to a greater extent and the polarized copy appears richer in contrast and detail. The fog, however, is not done away with.

While in the case of normal copies the latter may be removed with FARMER'S reducer³⁾, this treatment does not succeed in the case of polarization. The slight diffusion of this reducer discovered by W. SCHEFFER⁴⁾, by which the action slowly progresses downwards from layer to layer, at once accounts for this phenomenon.

Of more significance to our knowledge of the latent image is the so-called neutralization of solarization by retarded development. That the said phenomenon is regarded as such is only attributable to the ideas of solarization and of polarization being confounded.

Development is retarded either by decreasing the amount of alkali

“gar nicht zu reduzieren, während das kurz exponierte schon in allen Einzelheiten erschienen war. Nach einiger Zeit merkt man indes, dass auch auf der überbelichteten Platte ein Bild vorhanden ist; dasselbe sitzt nur in den *tieferen Schichten* allerdings als normales Diapositiv, d. h. noch nicht solarisiert. während in der Aufsicht erst nach längerer Entwicklung etwas zu sehen ist. Beim Fixieren merkt man deutlich, dass *in der obersten Schicht* der lange belichteten Platte kein Bild vorhanden ist, indem nach kurzem Fixieren das Bild auch in der Aufsicht kräftiger wird, offenbar weil das unreduzierte Jodsilber der obersten Schicht weggenommen wird”. (J. M. EDER, Jahrb. f. Phot. u. Repr. 1903; S. 46. Zeitschr. f. wiss. Phot. 1903; Bd. I; S. 17).

1) J. M. EDER. Handb. d. Phot. 1902; Bd. III; S. 115.

Phot. News. 1880; Vol. 24; p. 304.

2) J. M. EDER. Handb. d. Phot. 1902. Bd. III; S. 115.

3) J. M. EDER. Handb. d. Phot. 1902 Bd. III; S. 555.

4) Brit. Journ. of Phot. 1906; p. 964.

J. M. EDER. Jahrb. f. Phot. u. Repr. 1907; S. 26.

in the developer or by the addition of potassium bromide. That only the rapidity of reaction of the developer is reduced, I was able to ascertain by the so-called neutralisation of solarization with a developer (rodinal 1 in 10) at a lower temperature. First a normal copy is developed, which when development is continued, turns into a polarized one.

However, the normal copy obtained in this way, differs very much from an ordinary one. When viewed by light reflected at an angle, it is just in the densest portions that the surface is found to have the highest gloss; consequently here the grains do not lie against the surface. After the copy has changed into a polarized one, in which the polarized depth image predominates, the surface remains unchanged, and now shows the highest gloss in the clear portions. Consequently the surface image has not undergone a reversion of density proportions, from which it follows *that the normal copy obtained by retarded development must be the solarized image*¹⁾. *This cannot be ascribed to a change of the solarization, i.e. to a change in the substance of the solarized latent image.*

Consequently in the surface glass we have a means of ascertaining in the case of solarization, whether an agent reacts upon the substance of the latent image or upon the development. Thus I could ascertain *inter alia*, that chromic acid mentioned by J. M. EDER²⁾ and ammonium persulphate referred to by K. SCHAUM and W. BRAUM, which both exercise a hardening influence upon the gelatine, at the same time also react upon the substance of the latent image in the case of solarization, by which it is reduced to the substance of the ordinary latent image.

III. SABATIER'S *polarization*.

If during the development of a plate light is admitted, three different phenomena may occur:

1. If a very slight amount of light is admitted, the plate in the developer shows an increase of reducibility.

¹⁾ It stands to reason that during the appearance of the normal copy in the developer, consequently before polarization sets in, development of the non-solarized silver haloid in the lower layers may take place. Consequently it is better to say that the solarized image is only formed within a certain definite time of development.

²⁾ Phot. Korresp. 1902; S. 647.

J. M. EDER. Jahrb. f. Phot. u. Repr. 1903; S. 23.

J. M. EDER. u. E. VALENTA. Beiträge zur Photochemie. 1904; II; S. 168.

J. M. EDER. Handb. d. Phot. 1903. Bd. III; S. 828.

³⁾ Phot. Mitt. 1902; S. 224.

2. If more light is admitted the image partly disappears, and a more or less fogged plate is obtained with partly a normal and partly a polarized copy, which shows great resistance to further development.

3. If still more light is admitted, the copy is polarized.

This last phenomenon I call SABATIER'S polarization.

J. M. EDER ¹⁾ credits SABATIER with first observing it, and says that SEELY gave the following explanation of it: The beginning of the development takes place at the surface; by the secondary exposure this developing image is copied upon the silver haloid underneath it, and as this exposure is more powerful than the first, the second image also develops more strongly, and total polarization results.

From the experiments carried out by me it appeared that the secondary exposure stopped the development of the surface image, for by reflected light it was seen that it did not increase in density any more, while total development of the whole surface might be expected. In order to ascertain to what extent the copying action of the developing surface image is operative in polarization, I effected the secondary exposure, at the advice of P. H. EYKMAN, on the glass side of the plate.

The exposed plate was developed for a short time, and just after the appearance of the image it was, while still in the developer, covered with a piece of opaque, black paper, which was everywhere pressed tightly against the emulsion to prevent the formation of air-bells, from which uneven development might arise, and then the glass side was exposed to direct daylight. As the quantity of developer soaked up by the paper was small and the temperature was below the normal one, the plate, to save time, was put in the developer again in the dark room, great care being taken to prevent light from reaching the front of the plate. After fixation a polarized copy appeared.

This shows that the copying of the developing image at most acts a very secondary part in the appearance of polarization.

The latter can only be ascribed to the further development of the surface image being stopped, and to the reducibility of the silver haloid underneath it being increased. Consequently here again two images are formed, one under the other: at the top a normal copy of little density, and under it a polarized one of greater density, corresponding to that of the polarized copy in fig. 3 in the case of solarization.

¹⁾ J. M. EDER Handb. d. Phot. 1898; Bd. II; S. 82.

The similarity between SABATIER's polarization and solarization is so great, that R. LYLE¹⁾ attributed the phenomenon mentioned sub 2 to the first zero condition of JANSSEN's periodicities of solarization being reached²⁾. In one of my experiments it appeared to me that this similarity only existed in so far as no image was to be observed. The first zero condition is characterised by the maximum of density obtainable, whilst the plate in question remained very thin. Consequently the cause of the disappearance of the image cannot lie in this.

By transmitted light, too, the plate does not show polarization in the portions exposed most intensively by the primary exposure, but in the portions that received the smallest amount of light. (Therefore SABATIER's polarization cannot be ascribed to solarization). It is easy to understand that the relative liminal value of a lower layer is first reached in those portions where the absorption of the surface image is the least, and where this layer, at the same time, is situated nearest to the free surface. So in this case the copying quality of the surface image exercises its influence.

IV. Herschel's effect.

By HERSCHEL's effect I understand polarization by double exposure. It differs from polarization by solarization in that much smaller amounts of light-energy are sufficient to produce it, and in the reducibleness of the primarily exposed silver haloid decreasing at once on a secondary exposure.

The duration of the primary exposure must always exceed the liminal value of the plate. After the secondary exposure has exceeded a certain maximum (*the critical exposure*), the plate shows a normal copy again. The value of the critical exposure depends entirely on the primary exposure. This has led to the so-called CLAYDEN's effect³⁾ (black lightning) being looked upon as a new phenomenon of the photographic plate.

The first observation dates from 1839, and was made by J. HERSCHEL, who stated that the red and the yellow rays of the spectrum could

¹⁾ Phot. Centralbl. 1902; S. 146.

²⁾ Compt. rend. 1880; T. 90; p. 1447, T. 91; p. 199.

Moniteur de la Phot. 1880; p. 114.

Beibl. z. d. Annal. d. Phys. u. Chem. 1880; S. 615.

J. M. EDER, Handb. d. Phot. 1906; Bd. I; T. 2; S. 306. 1898; Bd. II; S. 78.

J. M. EDER, Jahrb. f. Phot. u. Repr. 1894; S. 378.

³⁾ J. M. EDER, Jahrb. f. Phot. u. Repr. 1901; S. 610.

Camera Obscura. 1901; bldz. 513.

J. M. EDER, Handb. d. Phot. 1906; Bd. I; T. 2; S. 312.

„ „ „ „ 1903; Bd. III; S. 834.

destroy the latent image of the blue and violet ones. At the same time a change in the degree of colour sensitiveness was ascertained. This was confirmed by CLAUDET ¹⁾, H. W. VOGEL ²⁾, W. ABNEY ³⁾, P. VILLARD ⁴⁾ and R. W. WOOD ⁵⁾. E. ENGLISCH ⁶⁾, H. W. VOGEL and W. ABNEY, however, considered this phenomenon to be solarization. An experiment published by P. VILLARD clearly shows that in the case of very advanced exposures the critical exposure does not appear any more, and the whole phenomenon coalesces with solarization. The highest sensitiveness of the plate is manifested towards red, the lowest to green.

WARNERKE ⁷⁾ observed HERSCHEL'S effect in images obtained by printing, and P. VILLARD, R. W. WOOD, R. LUTHER and W. A. USCHKOFF ⁸⁾ with Röntgen rays in the case of primary exposure. At the same time they demonstrated that the phenomenon did not appear if these exposures were reversed.

J. STERRY ⁹⁾ communicated another variety, viz. that certain kinds of chemical fog can be neutralized by weak light.

Some time ago one of my friends showed me a few camera exposures on EASTMAN films ¹⁰⁾, which I recognized as the phenomenon observed by J. STERRY. They had been exposed once, but had been in the camera for about 3 years without any precautions having been taken except that light had been prevented from reaching them. Consequently in this case the diffused exposure had been replaced by a chemical process of analysis, which had acted similarly, and had been exercised upon the silver bromide by the vapours given off by the celluloid, which had been diffused in the silver bromide gelatine.

Fig. 5 is an outdoor subject; it had a short exposure and shows various abnormalities. Nearly the whole copy is polarized, with the exception of the sky near α , where the critical exposure had been exceeded. The dogs in the foreground, reflecting the greatest amount of light there, show the beginning of the formation of a normal copy,

1) *Annal. d. Chimie et de Phys.* 1848; 3e série; T. XXII.

2) H. W. VOGEL. *Handb. d. Phot.* 1890!; Bd. 1; S. 221.

3) *Phot. Archiv.* 1881; S. 120.

4) *Soc. d'encourag. pour l'Industrie nation. Extr. d. Bulletin*; Nov. 1899.

5) *Astrophys. Journ.* 1903; Vol. XVII; p. 361.

6) J. M. EDER. *Jahrb. f. Phot. u. Repr.* 1902; S. 73.

7) *Phot. Arch.* 1881; S. 120.

8) *Phys. Zeitschr.* 1903; S. 866.

9) This paper I only know from a resumé in J. M. EDER. *Jahrb. f. Phot. u. Repr.* 1903; S. 425.

10) The lens of the camera was a slow aplanat, and was used with full opening for the interior; for the outdoor exposure it was stopped down.

and so do the shoulders of the female figure to the right, owing to which especially the left shoulder shows a false relief. Consequently the critical exposure is reached after the greatest transparency of the image has been obtained.

Between these beginnings of a normal copy and the polarized copy there is a clear strip, which is narrower where the exposure has been stronger. The dog to the left shows greater density of the normal copy than the one to the right, where the bright strip is broader. This strip occurs in the brighter parts in a manner that is the exact opposite of the way it occurs round the outlines of the leaves of the tree and of the bare trunk in the background; a few shoots are even quite white. Here the strips are found in the darkest parts, and decrease in width towards the right of the tree top, round which a smaller light intensity has been active.

The wall was more strongly lighted to the left than to the right, and appears slightly darker there, but still it remains polarized, which is easier to see in the original film than in the reproduction. The left side of the tree top shows more halation than the right, while no halation whatever is to be seen in the part of the sky near *a*, which was subject to the action of light with greater contrasts. Here, however, one would have expected that halation would have acted in the opposite direction, viz. not decreasing in density in the darkest portions, but increasing in the lighter ones.

The comparatively slight density of the sky near *a* is striking, and so is the low colour sensitiveness to green (grass and foliage), while the dark blond and dark brown hair of the two female figures show a stronger action of the light, which can be seen better in the original copy. The wall in the background is white, so that here the colour sensitiveness to the red of the bricks cannot be ascertained.

Fig. 6 renders the critical exposure still more strikingly. It represents an interior; the film was exposed a few seconds, and shows every object in the room polarized, even a large portion of the halation owing to the light from the left window. What is seen outside through the windows has been copied normally; here, consequently the critical exposure has been exceeded. The halation has partly made the lead setting of the coloured glass appear normal again, while to another portion it has given greater density owing to the action of the light being stronger. A large part of the right half and a smaller part of the left bottom section show differences in density, which must be ascribed to uneven action of the chemical reactions during the time the film was kept. Fig. 5 also shows this, but in a slighter degree; here, however, it is less noticeable on account of the wealth

of detail of the image. The action being slighter to the right, the images are seen to be thinner accordingly.

The same thing is to be observed in a Röntgenogram placed at my disposal by P. H. EYKMAN. The plate was exposed to Röntgen rays with a so-called intensification screen (calcium wolframate screen), and laid aside some time before development. Calcium wolframate postluminesces¹⁾ owing to which a plate is consequently further exposed. The objects photographed with Röntgen rays were a piece of bone, a piece of thin and a piece of thicker, insulated copper wire. Fig. 7 gives a reproduction of the negative. The places of the thin copper wire show development of the silver bromide which is nearly as strong as in the field, where the Röntgen rays and the luminescence together have acted most strongly. A narrow strip along the edge indicates how far the screen covered the plate; consequently there only the R. rays have acted. The place of the thin copper wire does not show a trace of development there; consequently the exposure remained below the liminal value.

The development of this place cannot be put down to irradiation through the screen; in that case the same thing would have to be observed in the case of the thick copper wire and the edge of the screen. Consequently the R rays must really have acted in such a way in that place, that the screen luminesced and this acted upon the silver bromide, while the exposure to R. rays remained below the liminal value.

P. H. EYKMAN also showed me a negative in the case of which the screen after irradiation had only been brought into contact with an unexposed plate²⁾. It showed a very thin image, from which it follows that the strongest action of the screen takes place immediately after the transformation of the absorbed Röntgen energy. Consequently if in the case of a röntgenogram with a calcium wolframate screen the action of the R. rays could be prevented, much shorter exposures would be sufficient to produce a good image. Hitherto this has proved to be impossible.

Another fact important for our knowledge of the latent image may be gathered from fig 6. The right bottom corner shows that the thinner the fog of diffused exposure becomes, the thinner also the polarized copy is. From this it follows *that in the case of secondary exposure the liminal value is lower than in the case of primary exposure, i.e. the amount of light necessary to effect the begin-*

1) Fortschr. a. d. Geb. d. R-Str. 1901; Bd. IV; S. 180.

2) The calcium wolframate screen was exposed to the R rays at the same time as the negative of Fig. 7.

ning of a decrease in reducibleness is smaller than is necessary for a beginning of an increase of this power with the original condition of the silver bromide.

V. The theory of the latent image.

In the case of the theory of the latent image two facts have to be observed, which are directly connected with each other:

1. The action of the light upon the silver haloids;
2. The physical or the physical and chemical changes in the silver haloid resulting from this action.

The theory proper of the latent image is only restricted to the latter, consequently comprises only secondary phenomena. Of all the theories enunciated, only the subhaloid theory of CHOISELAT and RATEL¹⁾ has maintained itself, especially owing to the subsequent investigations of M. CAREY LEA²⁾, H. WEISS³⁾, J. M. EDER⁴⁾, and others. While J. M. EDER⁵⁾ looks upon silver subhaloid as a molecular compound, M. CAREY LEA⁶⁾, E. BAUER⁷⁾, L. GUNTHER⁸⁾, and LÜPPO-CRAMER⁹⁾, consider it an absorption compound of colloidal silver and silver haloid, thus practically maintaining ARAGO's old silver-germ theory in a new shape. However, it is impossible yet to point out a single fact in photography from which it appears which of these two theories is to be preferred; all chemical reactions on the latent image might be accounted for by either theory and

1) Compt. rend. 1843: T. 16; Nr. 25.

” ” ” T. 17; Nr. 4.

J. M. EDER. Handb. d. Phot. 1898; Bd. II; S. 111.

2) Americ. Journ. of Science. 1887; Vol. 33; p. 349.

Phot. Korresp. 1887; S. 287, 344 u. 371.

3) Zeitschr. f. phys. Chemie 1905; Bd. 54; S. 305.

Chem. Centralbl. 1906; Bd. I; S. 807.

J. M. EDER. Jahrb. f. Phot. u. Repr. 1906; S. 473.

4) Sitzungsber. d. kaiserl. Akad. d. Wiss. zu Wien. Mathem.-naturw. Klasse.

Bd. CXIV; Abt. IIa; Juli 1905.

Zeitschr. f. wiss. Phot. 1905; Bd. III; S. 329.

J. M. EDER. Handb. d. Phot. 1906; Bd. I; T. 2; S. 277.

Phot. Korresp. 1905; S. 425 u. 476.

” ” 1906; S. 81, 134, 181 u. 231.

” ” 1907; S. 79.

5) See note 4.

6) See note 2.

7) Zeitschr. f. phys. Chemie. Bd. 45; S. 618.

8) Abhand. d. naturk. Ges. Nürnberg. 1904; Bd. 15; S. 26.

9) Phot. Korresp. 1906 u. 1907.

LÜPPO-CRAMER. Photogr. Probleme. 1907; S. 193.

neither of them has hitherto afforded a definite explanation of the various photographic phenomena.

As the photo-chemical process of analysis upon the silver haloid is only characterized by a continuous reduction process, it is quite natural to assume this also in the cases of the solarized latent image. Still there are a few phenomena which seem to contradict this.

Thus W. ABNEY¹⁾ assumed the formation of an oxybromide, and founded this assumption on the fact observed that potassium bichromate and potassium permanganate, perhydrol and a few anorganic acids promote solarization. The anti-solarizing action, also pointed out by him, of reducing agents, like pyrogallol, ferrous sulphate, ferrocyanide of potassium, nitrites, and sulphites, has only been judged from the appearance or non-appearance of polarization, and may be entirely reduced to retarded development.

LÜPPO-CRAMER²⁾ considers the oxidation theory of solarization absurd. He points to the solarization of the plate even if no oxygen is admitted, and to the circumstance that all the agents that prevent solarization, are halogen-absorbing substances. As a characteristic example he mentions silver nitrate, the anti-solarizing action of which is, according to him, to be ascribed to halogen-absorption, not to oxidation, and considers this action analogous to that of nitrites, sulphites and hydroquinone.

This view is at variance with his criticism of the oxidation theory, in which he also points to the continuous loss of halogen in the case of continued exposure of the silver haloid, and to his observation that a bromide solution counteracts solarization, and may even entirely neutralize the latent image³⁾. *Consequently halogen-absorption must promote solarization.* The promotion of solarization mentioned by W. ABNEY, and referred to above is not to be ascribed to oxidation, but to halogen absorption.

That oxidation of the substance of the latent image neutralizes solarization, has been ascertained by J. M. EDER⁴⁾ with his chromic acid reaction, and by K. SCHAUH and W. BRAUN⁵⁾ with their ammonium persulphate reaction. That in this case we really have not the

1) Proc. Roy. Soc. 1873; Vol. 27; p. 291 a. 451.

2) LÜPPO-CRAMER. Phot. Probleme. 1907; S. 138.

3) J. M. EDER, Jahrb. f. Phot. u. Repr. 1902; S. 481.

4) Phot. Korresp. 1902: S. 647.

J. M. EDER, Jahrb. f. Phot. u. Repr. 1903; S. 23.

J. M. EDER, u. E. VALENTA, Beiträge zur Photochemie. 1904; II; S. 618.

J. M. EDER, Handb. d. Phot. 1903; Bd. III; S. 828.

5) Phot. Mitt. 1902; S. 224.

phenomenon of retarded development I could observe through the formation of a dull surface image. Further LÜPPO-CRAMER¹⁾ proved that the silver subhaloid of POITEVIN's photochromics undergoes regression to silver haloid by oxidation. J. M. EDER²⁾ described the same thing in his investigations of the latent image with the nitric acid reaction.

Quite a different view of the progressive photochemical analysis of silver haloids, was given by H. LUGGIN³⁾. He stated that in the case of more intensive exposure, also a proportionately greater amount of formed silver haloid, under the influence of the increasing halogen pressure takes from the silver haloid the power of affording germ-points for the deposit of metal, and that consequently halogen-absorbents (chemical sensitizers) would be the best means of keeping the halogen pressure as low as possible, and so of preventing solarization. Consequently he considers solarization as a phenomenon consisting in the prevention of germ-formation. His statement: "The beginning of solarization may often be obviated by selecting smaller stops and increasing the exposure accordingly," is confirmed in the case of silver iodide gelatine⁴⁾.

Still this proposition that halogen absorption prevents solarization is at variance with what goes before. I have therefore investigated this matter more closely.

Silver haloid is decomposed by the action of light, but a polished silver bar exposed in the light to halogen vapours, at once combines with it to form halogen silver. Consequently in the presence of an excess of halogen the silver haloid is not decomposed.

A highly sensitive silver bromide gelatine plate, which was partly coated with collodion, was exposed to direct daylight. It was observed that the photo-chemical decomposition under the collodion remained considerably behind that of the free surface, and had not even increased appreciably after an exposure of several weeks. The violet brown discolouration appeared only at the free surface, and could be removed by the plate being rubbed carefully. A plate, exposed at the same time on the glass side, also showed retardation as to the photo-chemical decomposition process, and against the glass the silver bromide seemingly remained unaltered. Consequently the fact that halogen prevents diffusion counteracts decomposition. In the case of

1) Phot. Korresp. 1907; S. 439.

2) See note 4, p.

3) J. M. EDER, Jahrb. f. Phot. u. Repr. 1898; S. 162.

4) J. M. EDER, Handb. d. Phot. 1906. Bd. I; T. 2; S. 309.

LÜPPO-CRAMER, Phot. Probleme. 1907; S. 152.

an excess of liberated halogen the opposite reaction takes place, which is quite in accordance with the regression of the latent image by a bromide solution in the case of silver bromide, as found by LÜPPO-CRAMER.

The diffusion of liberated halogen will always take place in a smaller degree in the series chlorine, bromine, iodine, on account of the atomic weight rising.

H. LUGGIN's rule must, therefore, be modified to the effect that in the case of a certain definite light intensity the progressive and regressive reduction get into a condition of equilibrium, which is only got over by a loss of halogen (absorption by the chemical sensitizer and diffusion).

The same thing was said in other words before now by J. PRECHT¹⁾, but on the ground of the appearance of solarization.

With this modified proposition of H. LUGGIN the deviations²⁾ from R. BUNSEN's and H. ROSCOE's reciprocity rule³⁾ can be accounted for, to which also belong the phenomena in the case of silver iodide gelatine just mentioned.

The knowledge of the latent image is arrived at by development. While the exposure causes decomposition of the silver haloid accompanied by a quantitative increase in silver subhaloid, a decrease of reducibility appears during development after a certain maximum of exposure. The solarization phenomenon is, therefore, a development phenomenon in the sense that development, owing to the modified properties of the latent image, shows a change.

Consequently in order to account for solarization a knowledge of the nature of development is requisite. Without it solarization remains an unsolvable problem.

Two methods of development are distinguished: The physical and the chemical method⁴⁾. Physical development is characterized by a deposit of a reduced silver compound from the developer on the exposed silver haloid; chemical development by reduction of the exposed silver halogen itself.

1) Zeitschr. f. wiss. Phot. 1905. Bd. III; S. 75.

2) J. M. EDER, Handb. d. Phot. 1906; Bd. I; T. 2; S. 48 u. 49.

" " " " 1902; Bd. III; S. 228.

" " " " 1898; Bd. II; S. 3 u. 5.

Phot. Mitt. 1890; S. 261.

Proc. Roy. Soc. 1898; Vol. 54; p. 143.

3) POGGENDORF Annal. d. Phys. 1862; Bd. 117; S. 538.

4) J. M. EDER, Handb. d. Phot. 1898; Bd. II; S. 29.

" " " " 1906; Bd. I; T. 2; S. 250.

By W. OSTWALD¹⁾, K. SCHAUM and W. BRAUN²⁾ it was supposed that the reduction of the silver bromide with chemical development was in the first instance brought about by a minimum amount of silver bromide dissolving as positive silver- and negative haloid-ion, after which the reduced substance was precipitated upon the germs. LÜPPO-CRAMER³⁾ succeeded in showing that a number of developing processes which were formerly looked upon as being purely chemical in their nature, not only in reality proceed physically, but that every chemical development is also partly of a physical character. W. SCHEFFER⁴⁾ was the first to show by a microscopical investigation that the entire chemical development is physical in its nature, i.e. it is brought about by molecular attraction between the photochemically reduced silver haloid, the germ, and the reduced feeding-substance. This, consequently, accounts for the altered structure of the exposed silver bromide gelatine plate before and after development⁵⁾.

Still the development of the photographic plate by the so-called chemical method really shows a difference from the physical method. LÜPPO-CRAMER⁶⁾ succeeded in demonstrating that the substance of the image in the case of a negative developed by the so-called chemical method, still contained bromine by the side of ordinary silver, which bromine he supposed to be a constant solution of silver in silver bromide. From this he infers that during the development, beside the silver another intermediate product must originate. It is only natural to assume, on the analogy of the reduction process of the silver haloid to silver through subhaloid, that also in the case of so-called chemical development the reduction takes place in the same way. Thus it appears that between chemical and physical development there is only this difference that the former keeps the subhaloid in solution with more difficulty than the latter, owing to which perfect reduction cannot take place. This at the same time accounts

¹⁾ W. OSTWALD. Lehrb. d. allgem. Chemie. 1893; Bd. 2; S. 1078

²⁾ J. M. EDER. Jahrb. f. Phot. u. Repr. 1902; S. 476.

Phot. Mitt. 1902; S. 229.

³⁾ LÜPPO-CRAMER. Phot. Probleme 1907. S. 159.

⁴⁾ Phot. Rundschau 1907; S. 142.

Phot. Korresp. 1907; S. 384.

⁵⁾ S. E. SHEPPARD and C. E. K. MEES. (Zeitsch. f. wiss. Phot. 1905; Bd. III; S. 355) consider V. BELLACH's observation that the size of the grain of the developed image decreases during the drying of the emulsion, to be in accordance with G. QUINCKE's foam-structure theory of the silver haloid grains which, according to him, contain gelatine. The non-coalescence of the exposed with the developed grain shows the incorrectness of this view.

⁶⁾ Phot. Korresp. 1905 S 319

for the fact that the image developed with certain developers loses density in the fixing bath; this loss of density is analogous to what is observed in the case of P. O. P. papers with silver chloride.

This further explains another apparent contradiction. While with silver chloride a lower and with silver bromide a higher degree of sensitiveness to light is observed, in other words, while quantitatively the same photochemic decomposition of silver bromide takes place with less absorption of light energy than in the case of silver chloride the exact opposite is seen to take place with the increase in density during development, which has been pointed out by H. and R. E. LIESEGANG ¹⁾, KÖNIG ²⁾ and LÜPPO-CRAMER ³⁾. Considering that silver chloride possesses a higher solubility, resp. has the power of bringing a greater number of ions into solution than silver bromide, it is easy to understand that quantitatively reduction can take place in a larger measure per unit of time, notwithstanding silver chloride is a more constant compound than silver bromide.

With silver iodide the same thing is observed still better. The reducibleness, resp. solubility is still less in this case, which has often occasioned the unjustified conclusion, that silver iodide is less sensitive to light than silver bromide, while the exact opposite is observed in the case of daguerreotypy and the wet collodion process, since here the feeding substance for development is introduced from without. Accordingly LÜPPO-CRAMER could use with silver iodide developers like amidol potassium carbonate, triamidophenol, diamidoresorcin, and triamidoresorcin, which show a far too great rapidity of reaction for silver bromide plates.

The higher sensitiveness of silver iodide-bromide plates as compared with silver bromide plates, owing to which more detail can be obtained in the darkest parts of the image, may therefore be ascribed to the more rapid formation of germs in the case of silver iodide, while the silver bromide serves as feeding substance for the developer. This further appears from the optical sensitizing of silver iodide-bromide plates.

While silver bromide can easily be made colour sensitive, this is not the case with silver iodide, which has been pointed out by J. M. EDER ⁴⁾, LÜPPO-CRAMER ⁵⁾, and others. Still both may be dyed

¹⁾ Phot. Mitt. 1901; S. 362.

Phot. Wochenbl. 1901; S. 405.

J. M. EDER. Jahrb. f. Phot. u. Repr. 1902; S. 572.

²⁾ Phot. Korresp. 1903; S. 14.

³⁾ J. M. EDER. Jahrb. f. Phot. u. Repr. 1903; S. 401.

⁴⁾ J. M. EDER. Handb. d. Phot. 1906; Bd. I; T. 2; S. 269.

⁵⁾ J. M. EDER. Jahrb. f. Phot. u. Repr. 1903; S. 46.

1904; S. 390.

Zeitschr. f. wiss. Phot. 1903; Bd. I; S. 17.

by optical sensitizers, but in this case the silver iodide-bromide plate behaves more like a silver iodide plate.

At the 79th German Physical and Medical Congress held in Dresden in 1907 W. SCHEFFER¹⁾ communicated a solarization theory founded upon his microscopic investigations²⁾, which explains solarization in quite a simple way.

When the exposed silver bromide gelatine plate is being developed certain grains ("Ausgangskörner") send out germs, upon which the reduced substance is deposited, because other grains ("Nahrkörner", formerly called "Lösungskörner") are dissolved in the developer and cause the growth of the germs. In an overexposed emulsion too many germ-producing grains "explode", and an insufficient number of "feeding" grains remain, so that no image of sufficient density can be formed. Consequently this theory is founded upon the transition of "feeding" grains into germ-producing ones by exposure, or rather of silver haloid into silver subhaloid.

This theory cannot be reconciled to the fact found by J. STERRY³⁾, J. M. EDER⁴⁾ and LÜPPO-CRAMER⁵⁾, that solarization can also appear with primary fixation, for in this case the feeding substance is supplied from without. The same holds good with regard to daguerreotypy.

B. HOMOLKA's solarization theory⁶⁾: "In the decrease of the amount of silver bromide I recognize the primary cause of solarization", is irreconcilable to the above, not to mention the circumstance that these two theories cannot explain the second reversion of solarization, and cannot account for the fact that even with the strongest overexposures an excess of silver haloid, i. e. of feeding substance, can be proved to be still present in the emulsion.

From the solarization with primary fixation it therefore appears, that the silver haloid germ loses this germinating property on further exposure, i. e. through the continued photochemical decomposition it has passed into another subhaloid containing less halogen, which possesses no germinative property. O. WIENER⁷⁾ proved the possibility of the existence of more subhaloids. Let us call the first the α -silver subhaloid and the second the β -silver subhaloid.

1) Phot. Korresp. 1907; S. 487.

2) Phot. Rundschau. 1907; S. 65 u. 142.

Phot. Korresp. 1907. S. 233 u. 384.

3) J. M. EDER. Jahrb. f. Phot. u. Repr. 1899; S. 289.

4) J. M. EDER. Handb. d. Phot. 1906; Bd. I; T. 2; S. 312.

5) LÜPPO-CRAMER. Phot. Probleme, 1907; S. 150.

6) Phot. Korresp, 1907; S. 168.

7) J. M. EDER. Jahrb. f. Phot. u. Repr. 1896; S. 55.

The reappearance of reducibility in the case of continued exposure, the so-called second reversion of solarization might then again be attributed to a newly formed γ -silver subhaloid, or, as the third reversion has not been observed, to a metallic silver germ or what is also possible, to both.

It must be emphasized at the very outset, that it is by no means impossible that before the α -silver subhaloid one or more other subhaloids, richer in halogen, are formed, which possess no germinative property, for a primary exposure below the liminal value of the plate points to photochemical decompositions taking place through the occurrence of auto-sensitizing¹⁾, so that the liminal value cannot be considered identical with the photochemical induction. Nor must it be inferred from the above that the α - or the β -silver subhaloid does not consist of more than one silver subhaloid.

Consequently it appears from all this that sensitiveness to light and reducibility must on no account be identified, as is generally done.

The untenableness of the existing theories of HERSCHEL'S effect by CLAUDET, P. VILLARD, R. W. WOOD and WARNERKE is accounted for by this faulty identification of reducibility with sensitiveness.

For the appearance of HERSCHEL'S effect it is necessary that the primary exposure should exceed the liminal value of the plate. Consequently α -silver subhaloid must have been formed.

That by the secondary exposure a regressive reaction occurs between the α -silver subhaloid and halogen, cannot be assumed, because in the case of prolonged exposures HERSCHEL'S effect coalesces with solarization, in connection with which the formation of the β -silver subhaloid without germinative property has already been stated. The experiments of W. ABNEY mentioned above, also prove that halogen absorption promotes the phenomenon. Consequently the secondary exposure acts in such a way that the α -silver subhaloid formed photochemically by the first exposure is reduced to β -silver subhaloid more rapidly than it has been possible for an equal quantity of α -silver subhaloid to be formed afresh. (In this case it may happen that the silver subhaloid has already entirely been photochemically dissolved, before the silver haloid has been able to supply it). This appears from the discussion of fig. 6. The photochemical induction of the α -silver subhaloid is, therefore, lower

¹⁾ Vide: J. M. EDER. System der Sensitometrie phot. Platten. Sitzungsber. d. kais. Akad. d. Wiss. in Wien 1899; IIa; Bd. 108; S. 1407. J. M. EDER u. E. VALENTA. Beiträge z. Photochemie. 1904; Bd. II; S. 48.

than the liminal value of the silver haloid. *Consequently the α -silver subhaloid is a substance of greater sensitiveness to light than the silver haloid.*

If with the secondary exposure the amount of α silver subhaloid originally present is exceeded, a normal copy is obtained again. The critical exposure, therefore, is that secondary exposure by which the same amount of α silver subhaloid is formed as was present after the primary exposure. So the best gradation of the polarized copy in the case of HERSCHEL'S effect is obtained, if lower light intensities are employed, as is shown by experiments.

The amended proposition of H. LUGGIN states that with a certain definite light intensity the progressive and the regressive reaction in the silver haloid arrive at a state of equilibrium, if the liberated halogen is not removed. This removal of halogen, either by diffusion or by chemical sensitizers, is therefore of paramount influence upon the origination of HERSCHEL'S effect. Consequently the most successful experiment is obtained with an emulsion which immediately absorbs the liberated halogen, or what is better even, if between the primary and the secondary exposure the plate is put aside for a considerable time, by which the liberated halogen is diffused out of the emulsion. It is still simpler to treat the plate after the primary exposure with a halogen absorbent, as was done by W. ABNEY, and we therefore regard judson blue, mentioned by H. W. VOGEL¹⁾ as a substance probably behaving analogously.

Therefore the direct decomposition of the silver haloid by reducers as in the case of J. SERRY'S experiments and fig. 5 and 6, in which the liberated halogen enters into combination, acts so favourably upon HERSCHEL'S effect.

This makes P. VILLARD'S statement clear that not all emulsions are equally suitable for experiment, as in the various emulsions there are different chemical sensitizers (both in quality and in quantity).

At the same time the nature of the phenomena in the case of intermittent exposure becomes clearer now.

That the effect of development upon silver bromide gelatine (but not necessarily the photochemical decomposition) is always slightly less than with a continuous exposure of the same duration was observed by W. ABNEY²⁾, K. SCHWARZSCHILD³⁾, and others. Many

¹⁾ H. W. VOGEL. Handb. d. Phot. 1890; Bd. I; S. 221.

²⁾ Photography 1893; p. 682.

Phot. Archiv. 1893- S. 339.

J. M. EDER. Jahrb. f. Phot. u. Repr. 1894; S. 373.

³⁾ Phot. Korresp. 1899; S. 171.

beginners in photography have observed the same thing when having made two exposures of different objects on the same plate. In this case it is easy to observe that not the sum of the two images is obtained, but that in one place one object dominates, in another place the other object.

According to K. SCHWARZSCHILD the result in the case of the exposure being intermittent depends, *inter alia*, upon the relation between the interval and the duration of the separate exposures; the longer the interval the better opportunity the halogen has of escaping by diffusion, or of being absorbed by a chemical sensitizer, and the more readily the next exposure will photochemically decompose the α silver subhaloid germ, which is more sensitive to light than the silver haloid, into β silver subhaloid and halogen, owing to which the result of development, apart from the photochemical induction which is to be exceeded again, will remain below the sum of the components.

The difference in sensitiveness to light between silver haloid and the α silver subhaloid appears, according to the above experiments, to depend largely upon the kind of light with the secondary exposure. The less sensitive the silver haloid and the more sensitive the α silver subhaloid is to a given colour, the more pronounced Herschel's effect will be. The smaller this difference, the more rapidly the silver haloid will produce fresh α silver subhaloid germs; it is true, in this case polarization is observable, but the minimum reducibility is soon reached. Further this is, of course, also dependent upon the amount of α silver subhaloid, i. e. upon the duration of the primary exposure. Perfect neutralization of reducibility need not occur then.

Consequently the colour sensitiveness occurring in the case of HERSCHEL'S effect is to be ascribed to the colour sensitiveness of the α silver subhaloid. Not one of the theories of the latent image enunciated hitherto can account for the phenomenon in such a simple way as the subhaloid theory. The subhaloids are dyes of quite different colours from silver haloid, and consequently with quite different spectra, owing to which the possibility exists of quite different colour sensitiveness, as in fact actually appears from the experiments of O. WIENER²⁾.

P. VILLARD proved spectroscopically that the greatest difference between the liminal value of the silver haloid and the photochemical induction of the α -silver subhaloid is situated in the red

1) Probably these photochemical decompositions proceed according to an exponential formula.

2) J. M. EDER. Jahrb. f. Phot. u. Repr. 1896; S. 55.

and consequently that the α -silver subhaloid is a substance sensitive to red. If α silver bromide gelatine plate is exposed to the action of a continuous spectrum, the reducibleness in the case of increasing exposure will proceed from blue to red. While after development it is observed that with increased exposure the density of the plate increases about and in the spectral blue, the yellow, the orange, and especially the red obtain only very slight densities. Consequently it is evident that the cause why the density of the image in the red, yellow, and orange portions cannot increase above a maximum, which is very low, lies in the α silver subhaloid possessing a far greater sensitiveness to red than the silver haloid, so that very soon a state of equilibrium has been reached, in which in a progressive process as much α -silver subhaloid is formed as destroyed.

The substance of the developable latent image is considered identical with M. CAREY LEA'S photohaloid. Now how does this behave in red light?

M. CAREY LEA¹⁾ exposed his pink photohaloid to the action of a spectrum; while under all colours the photohaloid changed, it remained unchanged in the red. From this it appears that the subhaloid germ of the latent image must be another substance than M. CAREY LEA'S photohaloid.

The behaviour of Röntgen rays differs from that of other kinds of light. According to P. VILLARD, R. W. WOOD, R. LUTHER, and W. A. USCHKOFF they show no HERSCHEL'S effect in the case of secondary exposure. This cannot be ascribed to total non-sensitiveness of the α silver subhaloid to Röntgen rays. It is true, F. HAUSMANN²⁾ and others stated that Röntgen rays produced no solarization, and consequently that there was no formation of β silver subhaloid, but P. H. EYKMAN³⁾, and subsequently K. SCHAU and W. BRAUN⁴⁾ could show that they do. So the silver subhaloid is also sensitive to Röntgen rays, and the non-appearance of HERSCHEL'S effect must be put down to the cause that for Röntgen rays the silver haloid has a liminal value as great as, or greater than the photochemical induction of the α silver subhaloid. It is therefore assumed that in the case of röntgenography the intermittent exposure, apart from the photographic induction to be exceeded each time, does not produce a photographic effect that remains below that of a continuous irradiation.

¹⁾ Americ. Journ. of Science 1887; Vol. 33; p. 363.

²⁾ Fortschritte a. d. Geb. d. R.-Str. 1901; Bd. V; S. 89.

³⁾ Fortschr. a. d. Geb. d. R.-Str. 1902, Bd. V, Heft 4.

⁴⁾ Zeitschr. f. wiss. Phot. 1904; Bd. 1; S. 382.

From H. LUGGIN's modified proposition it appears clearly, how the chemical sensitizers promote the photochemical decomposition process of the silver haloids by halogen absorption. They consequently prevent regression.

LÜPPO-CRAMER ¹⁾ describes the following experiment, which confirms this. Precipitated silver chloride shows neither with silver nitrate, nor with ammonia, both chloride absorbents, any increased sensitiveness to light when photochemically decomposed; in an emulsion where the rapid escape of the liberated halogen is prevented, the action of the chemical sensitizer is therefore observed. From this it follows that the chemical sensitizer does not react upon the silver haloid itself at all.

Even from the considerable deviations from the reciprocity rule in a silver bromide gelatine plate with very low light intensities it follows that gelatine is not a chemical sensitizer, which has also been proved in another way, experimentally, by LÜPPO-CRAMER.²⁾

While the chemical sensitizers act very favourably in the printing-out process, they have no, or even a detrimental influence in the case of silver haloid emulsions intended for development, as has been pointed out by LÜPPO-CRAMER ³⁾. If it is borne in mind that the α silver subhaloid germ itself is a substance very sensitive to light, which with loss of halogen, passes into the β silver subhaloid without germinative property, it is clear that a too active chemical sensitizer does not promote reducibility.

A number of chemical sensitizers, however, are oxidizers at the same time. From what has been said above it has appeared that oxidation transforms the β silver subhaloid into α silver subhaloid (neutralization of solarization), which may be thus represented: β silver subhaloid + oxygen = silver oxide (Ag_2O ?) + α silver subhaloid.

This reaction seems to proceed very slowly in the case of sub-bromides.

Owing to this complications may arise, so that the chemical sensitizer, while on one hand promoting the photochemical reduction, on the other hand again partly oxidizes the silver subhaloid that has been formed. Here the action of the chemical sensitizer is favourable for the process of development, as in the case of the

¹⁾ Phot. Korresp. 1901; S. 224.

LÜPPO-CRAMER. Wissensch. Arbeiten 1902; S. 87.

J. M. EDER. Jahrb. f. Phot. u. Repr. 1906; S. 648.

²⁾ LÜPPO-CRAMER. Phot. Probleme. 1907; S. 33.

³⁾ Phot. Korresp. 1903; S. 25.

silver iodide collodion plate with silver nitrate, which in the presence of light is a powerful oxidizer¹⁾, and the question is whether the so-called neutralization of solarization by silver nitrate is not to be ascribed to this as well, and consequently is real neutralization.

If silver haloids are allowed to be photo-chemically decomposed, the great influence of the size of the grain at once becomes evident. While fine grain silver chloride or bromide is decomposed rapidly, the latter even more rapidly than the former, the directly visible decomposition in the case of course-grain silver haloids is slower. This can at once be accounted for by H. LUGGIN's modified rule. At the surface of the silver haloid grain the liberated halogen can escape more easily, or enter into composition; inside the grain it acts regressively, so that the progression will decrease from the surface to the centre.

H. LUGGIN²⁾, too, refers to the same thing in the case of silver iodide. But even if it is in a very finely divided condition, the directly visible photo-chemical decomposition does not take place rapidly. Owing to its greater atomic weight the liberated iodine not only diffuses more slowly, but moreover it is a solid substance. By absorption of this iodine, e. g. by silver nitrate, the directly visible photo-chemical decomposition at once becomes more rapid, so that it is clear why a silver haloid which is more sensitive may all the same yield a less advanced photo-chemical decomposition.

The surface decomposition of the silver haloid grain at the same time points to the fact that here, too, the seat of the latent image is to be looked for. This is also to be inferred from further data. Thus the deposits of reduced silver haloids discovered by W. SCHEFFER³⁾ always start from the surface of the silver haloid grain, which appears from a microphotograph published by him. Further LÜPPO-CRAMER⁴⁾ pointed to the dependence of the quantity of dye in the case of optical sensitization upon the surface to be coloured (i. e. upon the size of the grain) with silver chloride and silver bromide.

When it has been pointed out that in the appearance of solarization by primary fixation and secondary development the existence of a

¹⁾ M. CAREY LEA (Phot. Korresp. 1887; S. 346) and LÜPPO-CRAMER (Phot. Korresp. 1907; S. 538) showed that silver subiodide is a substance which is extremely easily oxidized.

²⁾ Zeitschr. f. phys. Chemie. 1897; Bd. 23; S. 611.

³⁾ Phot. Rundschau. 1907; Heft 6.

⁴⁾ J. M. EDER. Jahrb. f. Phot. u. Repr. 1902; S. 58.

„ „ „ „ „ „ 1905; S. 61.

silver subhaloid can be proved, this is not enough to account for the solarization phenomenon.

In order to illustrate this let us assume a photo-chemical decomposition with direct recombination of the liberated halogen.

If the exposure of a photographic plate is prolonged, the silver haloid will keep forming α silver subhaloid, which is the germ for development. From HERSCHEL's effect, however, it appears that this α silver subhaloid in itself is a highly light-sensitive compound, so that it is not to be assumed that a continual accumulation of germs is taking place. Consequently the α silver subhaloid rapidly decomposes into β silver subhaloid and halogen. At the surface of the silver haloid grains a condition therefore arises in which the number of germs present depends upon formation and destruction.

If the quantity of the remaining grain surface silver subhaloid decreases, the quantitative formation of α silver subhaloid will also decrease, and as the latter itself is highly sensitive to light, the consequence of this will also be a quantitative decrease of the number of remaining germs, in other words, the reducibleness will decrease, i. e. solarization will set in.

This phenomenon is, therefore, entirely dependent upon the available surface of the grain (size of the grain). In his experimental researches LÜPPO-CRAMER¹⁾ repeatedly pointed to this fact.

In reality this, of course, does not take place so rapidly. The various makes of plates have chemical sensitizers which differ from each other (qualitatively and quantitatively). This, together with the prevention of diffusion, is the reason why the different commercial plates begin to get solarized after mutually different exposures.

The thiosulphate reaction shows peculiarities which can be accounted for now. The subhaloids are decomposed by the action of thiosulphate into silver and halogen silver, which after being converted into silver thiosulphate, dissolves as a double salt. The place of the α silver subhaloid germ and the β silver subhaloid is consequently taken by silver, which also possesses the property of germination, as appears from the development of primarily fixed plates. Strong solarization, however, still produces solarization during development after primary fixation, so that the reaction between β silver subhaloid and the thiosulphate in the binding material is a slow one, as is the oxidation process already referred to. So if a highly sensitive course

¹⁾ Phot. Korresp. 1901; S. 350.

LÜPPO-CRAMER. Wissensch. Arbeiten. 1902; S. 41.

LÜPPO-CRAMEB. Phot. Probleme 1907; S. 146.

grain plate, i. e. one with a small grain surface, in other words, with a small quantity of β silver subhaloid, which has been exposed till solarization has set in, is treated, the reaction in the gelatine will be complete sooner than with a greater quantity of β silver subhaloid in the same gelatine plate, as is the case with fine grain emulsions. The reducibleness will consequently show an increase (not to be confounded with acceleration), so that in proportion to the strength of the thiosulphate solution employed, and the duration of the action, the solarization will be removed, either to a smaller or to a greater extent, or totally.

This phenomenon was observed experimentally by KOGELMAN¹⁾, VIDAL,²⁾ and E. ENGLISCH³⁾, while LÜPPO CRAMER⁴⁾ could not demonstrate solarization at all with primarily fixed, highly sensitive, coarse-grain plates, which fix more slowly than fine-grain ones.

Sulphocyanides act analogously in reducing solarization.

In the case of SABATIER'S polarization the strong decrease (disappearance?) of development of the image after it has appeared is not to be ascribed to the decrease of the number of germs, as they have already fulfilled their function⁵⁾. So the decrease of development can only be a reduction of the speed of development, which is to be accounted for by a strong decrease in the supply of feeding substance. From the theory given above of the so-called chemical method of development it has appeared that the silver subhaloid proves to be less soluble in the developer than the silver haloid. Therefore the more soluble silver haloid can, after reduction, be precipitated upon the germ, which still remains unchanged in its place. Consequently if the secondary exposure is of an intense nature, the feeding substance will be enveloped by subhaloid, by which development is retarded. This will take place in the developer all the more readily, because it is an absorbent of halogen.

In conclusion reference may be made to a possible explanation of the variations in the optical sensitizing of the photographic plate which is characterized by a considerable decrease in reducibleness being noticeable in the places where the power of absorption is spec-

1) J. M. EDER. Jahrb. f. Phot. u. Repr. 1895; S. 419.

2) Bull. Soc. franç. Phot. 1898; p. 583.

3) J. M. EDER. Jahrb. f. Phot. u. Repr. 1901; S. 608.

" " " " " " 1902; S. 79.

" " " " " " 1904; S. 423.

4) LÜPPO-CRAMER. Phot. Probleme. 1907; S. 150.

5) So far there is not a single reason for assuming that this reduced substance consists exclusively of α silver subhaloid germs, which pass into β silver subhaloid by the secondary exposure, by which further development would be checked.

trally highest. From M. ANDRESEN's experiments ¹⁾ it appears that the photo-chemical decomposition products remain in contact with the dyestuff, so that the α silver subhaloid obtains a different colour sensitiveness. In this case complications may occur, if the dye is at the same time an absorbent of halogen (a chemical sensitizer), by which it changes or loses its absorption spectrum, and a consequent promotion of the photo-chemical decomposition action sets in.

VI. *Conclusions.*

From what has been said a few conclusions may be drawn, which may be of importance in practice.

Both α silver subbromide and iodide are substances of a much greater sensitiveness to light than the corresponding silver haloid.

Consequently if it was possible to compose emulsions in which these substances were present side by side with the silver haloid which as feeding substance is indispensable for development, plates would be obtained not only of a higher sensitiveness than the present ones, but in them a chemical sensitizer would be practically desirable in every respect to prevent regression. Such plates would entirely comply with the reciprocity rule, and would render the light gradations of the objects to be photographed much more correctly, which may be of great value to astronomical photography, e.g. for the determination of the light intensity of stars by the photo-chemical method (Photometry).

The α silver subhaloid can be optically sensitized, so that its application might obtain a great extension. The exact colour sensitiveness of the α silver subhaloid separately is not yet known exactly. (That in the case of secondary exposure the highest sensitiveness is situated in the red, the lowest in the green, points with great probability to the α silver subhaloid being a green substance). The experiments mentioned indicate everywhere only the difference in light sensitiveness between silver haloid and the α silver subhaloid. The greater this difference, the more favourable the result obtained. Consequently the best expectations might be entertained with respect to silver chloride plates with α silver subiodide, and it is an open question whether the latter may not be allowed to ripen too. The β -silver subhaloid seems to possess, photo-chemically, an extremely low sensitiveness, which can only be advantageous in practice.

This process yields directly polarized copies (positives through the

¹⁾ Phot. Korresp. 1898; S. 504.

camera). On one hand this seems an objection, as all printing methods are based upon the production of normal copies (the negative process). But it should be borne in mind that hitherto very few researches have been made in this domain.

For direct colour photography¹⁾ with colour elements lying side by side under the emulsion, according to L. DUCOS DU HAURON's system (which especially lately has given promise of a great future), which requires directly polarized copies, and which so far has only succeeded in obtaining them in an indirect way, this method would also be practically valuable.

In this direction little experimenting has hitherto been done from a photo-chemical point of view, and even in what has been done it has been impossible to account for the phenomena that occurred, so that for the present there is no need for us to take too pessimistic a standpoint with reference to this.

VII. *The shape of the image in the case of Herschel's effect.*

As to the shape of the image in the case of HERSCHEL's effect fig. 8 may be referred to.

It is clear that after the critical exposure the normal copy is again a surface image. If a considerable portion of the surface silver haloid present has already been decomposed into α silver subhaloid and halogen, the secondary exposure will not be able again to form as much α silver subhaloid as would have been the case if the primary exposure had not taken place. A negative is obtained then the density of which is less than that of a plate not previously exposed. This case presents itself in the sky α in fig. 5.

Advanced primary exposure may result in solarization, in which case the surface silver haloid can no longer supply the same quantity of germs as was present before: HERSCHEL's effect then coalesces with solarisation, and the critical exposure can no longer be ascertained.

The greater light sensitiveness of the α silver subhaloid as compared

¹⁾ I expressly call this method "direct", because I cannot agree to the judgment of a number of others, who want to classify it among the indirect methods. They say that it is not direct colour photography, but three-colour photography, ignoring the fact that the bleaching method which is reckoned to belong to the direct methods, is also three-colour photography. Nor can I agree to A. v. HÜBL's classification (Phot. Rundschau, 1908, p. 2), by which the bleaching process would be assigned to the indirect methods. The fact of the matter is that the difference is only a question of method, i.e. whether the colours are obtained directly after exposure (with development), or only through subsequent addition.

properties of the latent image."

a



Fig. 5.

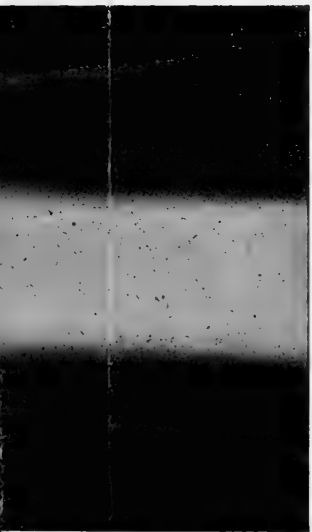


Fig. 7.

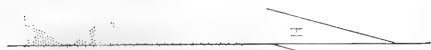


Fig. 1.

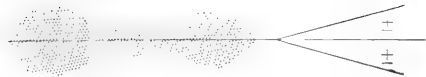


Fig. 2.



Fig. 3.

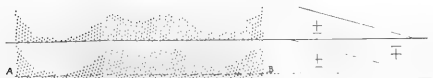


Fig. 4.



Fig. 5.



Fig. 6.

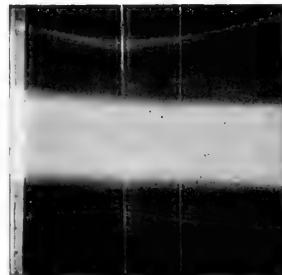


Fig. 7.

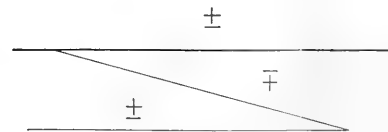


Fig. 8.

with that of silver haloid is also shown in the amount of halation. In fig. 5 the foliage of the tree is affected by it, while the houses round the sky near a do not show any; there the halation was too slight to exceed the liminal value of the silver haloid. In fig. 6 the dark lead frame of the window also shows the destruction of the germ owing to halation; on the other hand on the right side it was able to form fresh germs through a more powerful action.

That the difference in light sensitiveness between the germ and the silver haloid is great, appears from the backs of the dogs, and from the shoulders of the female figure to the right in fig. 5. The narrow white strip indicates that after the germs had been totally destroyed at the free surface, for some time longer the silver haloid again began to supply germs, first in the most strongly exposed portions, and then gradually also in those which received less exposure. Consequently if the action of the light increases, these strips must become narrower, which is also shown by the figure, as the dog to the left was more glossy than the one to the right.

The white strips along the edges of the black objects in the background are of quite a different nature. These are to be ascribed entirely to irradiation, for in the case of stronger light intensities occurring side by side they are broader than where the intensity is less great.

If observed very closely by light reflected at an angle, these bright strips are seen to possess a greater gloss than the portions immediately adjoining them. To the left of the tree top this is easier to see than to the right. The light from the wall has acted more intensely to the left than to the right, and notwithstanding the polarization a copy of greater density is shown there. That the critical exposure should have been surpassed, is out of the question here.

This phenomenon, too, can be accounted for according to the theory given, for in this theory it has been stated, that the critical exposure is not surpassed till the secondary exposure has formed a greater amount of α silver subhaloid than is present in consequence of the primary exposure. Consequently after the liminal value of the silver haloid has been surpassed, a new surface image can originate, the density can increase afresh, and still at the same time the copy will remain polarized.

All the abnormalities in the figures 5 and 6 have thus been accounted for.

In conclusion I wish to express my best thanks to Mr. P. H. EYKMAN for finding materials and placing them at my disposal, and for his constant interest in my work.

Physics. — “*Isotherms of diatomic gases and their binary mixtures.* VIII. *The breaking stress of glass and the use of glass tubes in measurements under high pressure at ordinary and low temperatures*”. By Dr. H. KAMERLINGH ONNES and Dr. C. BRAAK. (Communication n°. 106 from the Physical Laboratory at Leiden by Dr. H. KAMERLINGH ONNES).

(Communicated in the meeting of April 24, 1908).

§ 1. *Introduction.* With former determinations of isotherms (Comms. nos. 78 April 1902, 97^a March 1907, 99^a Sept. 1907, 100^a and 100^b Dec. 1907, 102^a Dec. 1907 and 102^b Febr. 1908) we could not raise the pressure above 60 atm. For in order to reach the required accuracy of about $\frac{1}{2000}$ we want a manometer which is reliable to the same degree. And till now we could only reach this degree of accuracy by means of a calibration with the open manometer described in Comm. n°. 44 (Nov. 1898) which reads to 60 atm. only. Already long ago we intended to include the higher pressures in our investigation. As a first step in that direction we have raised the upper limit of the pressure to 120 atmospheres. For while keeping the same arrangement we could easily complete the existing open manometer to one of the same accuracy reading to 120 atmospheres by merely adding a number of new manometer tubes of greater resisting power than those we had.

The new manometer and also the other apparatus intended for pressures to 120 atmospheres are nearly completed and will soon enable us to determine the isotherms to 120 atm. Afterwards we hope that these will be followed by measurements at still higher pressures. It seems even possible to reach 500 atmospheres with almost the same accuracy.

For all these investigations it is a great advantage when the piezometer- and barometer tubes can be made of glass. Therefore we have investigated in how far this would be possible with regard to the breaking stress of glass.

The breaking stress of glass has been investigated most at ordinary temperature, because it is in the first place desirable that the reservoirs of the manometer tubes of the open manometer and the divided stems of the piezometer tubes should be made of glass.

To these measurements we have added a series of determinations at lower temperatures in order to judge to what extent glass piezometer reservoirs could be used for the higher pressures at these temperatures.

Investigations on the maximum strain of glass have been made by GALITZIN¹⁾ and by WINKELMANN and SCHOTT²⁾. The former has determined the inner pressure which cylindrical glass tubes can resist, the latter two have determined the maximum strain of glass rods. GALITZIN's determinations, however, were made only at relatively small pressures, those of WINKELMANN and SCHOTT only at ordinary temperature.

In our investigation we partly follow the method of GALITZIN. From the theory of elasticity we can derive in connection with the dimensions of the apparatus the maximum tension in the glass from the maximum pressure which the glass tube resists. The results obtained in this way were compared with the direct data obtained in a second series of measurements, where the maximum strain of glass rods was determined. If we take into consideration the material investigated, it is not astonishing that the results of the two series show irregular differences. These differences however are of no influence upon some general conclusions that may be drawn from the measurements.

§ 2. *Determinations at ordinary temperature.*

Survey of the observations and arrangement of the measuring apparatus.

1. *Determination of the maximum inner pressure.*

The experiments were made with ordinary Thüringer glass. A cylindrical reservoir of the glass to be investigated was fused on to a thick walled glass capillary. The capillary was provided at its end with a steel nut with a hexagonal part by means of which it could be screwed on to a steel capillary which is connected to a pressure pump with a metal manometer. For measurements to 200 atms. it was fixed on the glass by means of sealing wax, for higher pressures it was soldered to the glass (comp. Comm. N^o. 99^a § 15, October 1907). If carefully made this connection proved able to resist the highest pressures (1200 atms.) The tubes were previously annealed carefully.

According to their dimensions they can be divided into three kinds:

- a. thick-walled tubes with large inner bore.
- b. thick-walled capillaries.
- c. thin-walled tubes with large inner bore.

It will appear that these three kinds of tubes give results different for each group.

¹⁾ Bull. de l'Acad. Imp. des Sciences de St. Pétersbourg, V^e Serie, B. XVI N^o. 1.

²⁾ Wied. Ann. 51.

The accuracy of the manometer is about 2%, which is quite sufficient for our purpose.

2. *Direct measurement of the maximum strain T_m by the determination of the breaking stress.*

In order to prevent as much as possible unequal strain during the suspension we have used here glass threads of at the most 0.6 mm. thickness¹⁾.

In order to reduce the tensions to minimum the glassrod was bent to a hook at either end. It was then suspended by the upper hook and the rod was drawn out in the middle to a thread by applying a certain force to the lower hook in about the same way as in the actual experiment. The weight used was a beaker into which water flowed.

§ 3. *Results.*

1. *Determinations with cylindrical tubes and internal pressure.*

In order to facilitate a comparison with GALITZIN'S results we take the same value $\frac{1}{4}$ for the coefficient of contraction. Let P_m be the maximum internal pressure, $2R$ the external diameter, $2R'$ the inner diameter (this is further on expressed in mm), and let $n = \frac{R}{R'}$, then we can represent the maximum tension T_m in the glass, (in this case that of the internal portions of the glass in a direction perpendicular to the axis of the cylinder) by:

$$T_m = \frac{1}{4} \left\{ 5P_m + 7 \left(\frac{P_m - 1}{n^2 - 1} - 1 \right) \right\}.$$

If, as is the case in the following tables, P_m is expressed in atmospheres, we find T_m expressed in KG/mm^2 (as it is given in the following tables) by multiplying the value found above by 0.01033.

For the three series mentioned in § 2 sub *a*, *b* and *c* the results have been combined in the table below. The meaning of the columns will be clear after what has just been said. Where several results are given under one number we have after the tube had partly burst (for instance so that only the end had broken off, or the tube had broken near the steel piece) used the same tube again for the following experiment.

The results for T_m are lowest for series *a* and highest for series *b*. In the last series this is especially the case for the tubes with a very

¹⁾ In the experiments of WINKELMANN and SCHOTT where thicker rods of 10–20 mm². section were used this required great care.

TABLE I. Maximum internal pressure and tension of cylindrical glass tubes.					
No.	$2R$	$2R'$	n	P_m	T_m
Series <i>a</i>					
1	9.3	3.5	2.66	340	5.38
2	8.8	4.0	2.20	280	4.91
3	8.7	4.2	2.07	230	4.21
4	9.4	3.2	2.94	270	4.10
5	9.2	3.0	3.07	380	5.70
6	9.7	4.2	2.31	370	6.30
7	10.4	4.0	2.60	240	3.83
8	12.8	5.8	2.21	260	4.54
9	17.6	5.0	3.52	290	4.19
Series <i>b</i>					
10	7.4	1.00	7.40	510	6.74
11	6.8	1.00	6.80	420	5.57
12	7.5	0.27	27.78	460	5.93
13	6.5	0.35	18.57	500	6.46
14	6.7	0.24	27.92	540	6.97
				800	10.33
				1100	14.21
15	6.7	1.08	6.20	530	7.08
16	5.9	0.70	8.43	680	8.94
17	5.8	0.46	12.61	1200	15.61
18	5.9	0.62	9.52	820	10.74
19	5.3	0.46	11.52	920	11.99
20	5.5	0.46	11.96	1060	13.80
21	6.6	1.00	6.60	660	8.78
22	7.2	1.40	5.14	520	7.07
23	6.4	1.35	4.74	520	7.13
Series <i>c</i>					
24	3.8	2.42	1.57	283	7.12
25	5.6	4.00	1.40	193	6.09
26	6.4	4.78	1.34	221	7.84
27	6.9	3.91	1.76	329	7.06
28	7.4	5.11	1.45	179	5.21
29	7.9	5.46	1.45	157	4.57
30	3.5	2.26	1.54	261	6.78
31	6.8	5.13	1.32	203	7.52
32	7.4	5.19	1.43	201	6.04
33	6.8	5.78	1.18	66	3.83
34	3.8	2.42	1.57	377	9.49
35	3.8	2.50	1.52	277	7.36
36	6.0	4.37	1.37	179	5.96
37	6.8	5.17	1.31	159	6.02
38	6.8	4.85	1.40	169	5.33
39	7.3	5.62	1.30	109	4.22
40	7.8	7.31	1.067	54	7.60

small inner bore if we except nos. 12 and 13 where the soldering was ineffective. Helped by the experience made we have treated the following tubes more carefully. With the tubes which have burst under a too low pressure the existence of irregular tensions appears clearly from the way of bursting, where the break has a transverse or irregular direction and not, as theory requires, parallel to the axis.

2. *Maximum strain of glass threads.*

The diameter of the threads lies between 0.1 and 0.6 mm. The results are combined in the two following tables. The bore was determined by a measurement of the diameter in two directions at right angles. The mean of these two measurements is given in the tables. The first table contains the results obtained with glass threads which have undergone only the operation mentioned sub § 2. To investigate the influence of irregularities which thus may remain in the structure of the glass we have made a series of measurements by means of threads which had beforehand been heated to incandescence and then cooled very slowly. The results of this series are combined in table III.

Stress in grams	Diameter in mm	T_m in KG/mm^2	Stress in grams	Diameter in mm.	T_m in KG/mm^2
257.6	0.119	23.1	2615	0.424	18.4
496.5	0.192	17.5	2785	0.446	17.8
457.8	0.159	22.9	1425	0.351	14.7
2325	0.384	19.8	1635	0.370	17.5
4175	0.257	22.7	1325	0.325	16.0
1475	0.325	17.6	1555	0.298	22.4
1695	0.311	22.4	2335	0.370	21.5
4105	0.487	22.1			

Except the thread for which T_m is lowest viz. 14.7 all the threads of table II show where broken a sharply ridged structure while we find at the edge a small semicircular smooth spot as was found by WINKELMANN and SCHOTT¹⁾.

¹⁾ p. 718 loc. cit.

TABLE III. Maximum strain of cooled glass threads.

Stress in grams	Diameter in m.m.	T_m in $KG./mm^2$	Stress in grams	Diameter in m.m.	T_m in $KG./mm^2$
2920	0.438	19.4	1940	0.325	23.4
3530	0.597	12.6	1760	0.322	21.6
2120	0.532	9.5	2850	0.445	18.3

With regard to the series of table III we may remark the following. In order to prevent changes of form of the threads suspended in the furnace and softened by the heat under the influence of gravitation, which afterwards during the measurements might give rise to irregular tensions, we have shaped the extremities (cf. § 2) not into hooks as in the former series but to closed rings in such a way that the whole becomes as symmetrical as possible with regard to a plane through the longitudinal axis. A comparison of the tables II and III shows that the two methods lead to the same results.

Of the glass thread with the lowest T_m (cf. table III) the section was little ridged but smooth, to the next value of T_m ($= 12.6$) belonged a relatively large smooth semicircular spot, while for the highest T_m ($= 23.4$) no spot was to be seen, but the whole section showed a very sharply ridged structure. All these facts agree with what has been found by WINKELMANN and SCHOTT²⁾.

On the plate we show the structure of the sections of a couple of threads at the place where the thread has broken. They both clearly show the smooth parts and the structure radiating thence. The smallest diameter of the sections is 0.530 and 0.555 mm. respectively.

§ 4. Conclusions.

Table I shows that as to the series *a* and *c* our results agree tolerably well with those of GALITZIN¹⁾.

Those of the series *b*, however, show that the result derived by him for the maximum internal pressure, viz. 623 atms. is too low, because the highest pressure observed by us is 1200 atms. For the tubes of the series *b* T_m appears to lie higher than would be expected from the observations in the two other series. Probably this must be explained as follows. From a comparison between the 3 series

¹⁾ loc. cit.

²⁾ Table I p. 12 and 13, loc. cit.

it appears that series *a* gives the lowest results for T_m , series *b* the highest. The fact that the values for *a* are lower than for *c*, must probably be ascribed to the circumstance that with almost equal internal bores the wall is thickest for the first series and hence the chance of abnormal stresses is greater. For series *b* the wall is thicker than for *c*, but the inner bore is much smaller, and hence the existence of inequalities and scratches on the surface which unfavourably influence the breaking stress¹⁾ are reduced to a minimum. For the tubes for which $2R' = 1$ mm. it seems that the two factors neutralize each other, for those with the smaller inner bore the favourable influence of the surface being smaller preponderates.

In order to investigate in detail in how far the above mentioned two unfavourable factors influence T_m we have applied the direct determination with thin glass threads of which the surface is as smooth as possible and where owing to the small bore abnormal tensions are necessarily small. The results which are much higher than those of WINKELMANN and SCHOTT, agree with those found by means of the first method and seem to justify the supposition made above about the unfavourable influence of a not perfectly smooth surface and inner abnormal stresses. They point to an upper limit for $P_m = 1700$ atms.

§ 5. *Determinations at low temperatures.*

The determinations in liquid air were made in the same way as those at ordinary temperature. The lower hook of the glass thread was fastened to a wooden bearer, placed beside the thread in a vacuum glass with liquid air. The first determinations gave results which differed much from the later ones. Their mutual agreement is very bad and they are characterized by very high values for the maximum strain, which vary from 44 to 73 KG. per mm.² while for the ordinary temperature the highest strain was 23 KG. per mm.². Also the structure of the section was totally different, being scarcely ridged but smooth. The smooth spot on the section was as a rule missing. In these measurements the threads were pulled asunder almost immediately after they had been placed in liquid air. Before the following measurements they were left at least 20 minutes in the bath of low temperatures. The latter gave lower results with a better mutual agreement. The structure of the section is similar to that at ordinary temperature, generally a little less distinct. The results are combined in the following table.

¹⁾ Cf. WINKELMANN and SCHOTT, loc. cit.

Dr. H. KAMERLINGH ONNES and Dr. C. BRAAK. Isotherms of diatomic gases and their binary mixtures. VIII. The breaking stress of glass and the use of glass tubes in measurements under high pressure at ordinary and low temperatures."

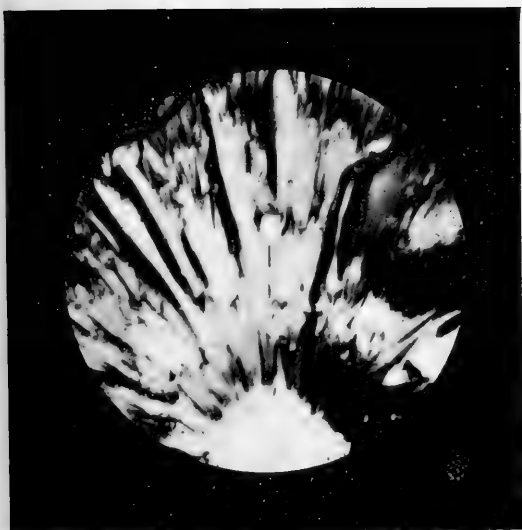


Fig. 1.



Fig. 2.



TABLE IV. Maximum strain of glass threads at the temperature of liquid air.

Stress in grams.	Diameter in mm.	T_m in KG/mm^2	Stress in grams.	Diameter in mm.	T_m in KG/mm^2
1993	0.280	32.4	2498	0.297	35.9
2653	0.372	24.3	2055	0.286	31.9
2523	0.290	38.2	3550	0.359	35.4
1253	0.276	29.5	3865	0.396	31.3

The results are still much higher than for the ordinary temperature, a very favourable result for measurements at low temperature.

Lastly a single determination in liquid hydrogen was made. Fifteen minutes after the thread had adopted the temperature of the bath it was pulled asunder. The total weight was 3013 grams, the diameter 0.271 m.m., hence the maximum strain in $KG/mm^2 = 52.1$ again much higher than at the temperature of liquid air. The structure of the section was striated, unridged and no smooth part occurred.

Zoology. — “*Poterion a Boring Sponge.*” By Prof. G. C. J. Vosmaer.

(Communicated in the meeting of May 30, 1908).

In 1822 HARDWICKE published ¹⁾ a short notice on a remarkable “Zoophyte, commonly found about the Coasts of Singapore Island.” The author stated that it belonged to the Sponges, and called it *Spongia patera*. Evidently not acquainted with this publication SCHLEGEL 1858 ²⁾ proposed the name *Poterion neptuni* for a sponge, which universally is considered to be identical with HARDWICKE’s sponge. According to the rules of nomenclature the object has, consequently, to be called *Poterion patera* (HARDW.), as first pointed out by SOLLAS ³⁾.

Both HARDWICKE and SCHLEGEL state that the sponge is fairly common. No wonder that this object, which presents itself as a gigantic cup, with a height of more than 1 M. and an aperture of 30 cm. or more, drew the attention of sailors. It is also found in many museums, especially in Holland. The Leyden Museum of Natural History, the Museum of the Utrecht University and the Museum of the Amsterdam Zoological Gardens (“Artis”) possess beautiful specimens, together more than 30. This rich material induced HARTING

¹⁾ Asiatic Researches XIV, p. 180.

²⁾ Handleid. Dierkunde II, p. 542.

³⁾ Ann. en Mag. Nat. Hist. (5) VI, p. 441 (1880).

to study the sponge, as far as the dry specimens allowed it. HARTING published in 1870 his well-known "Mémoire sur le Genre Poterion",¹⁾ the result of an examination of 27 specimens. Since that time the sponge has hardly been mentioned. It seems indeed strange that since SCHLEGEL's publication — half a century ago — these gigantic specimens which obviously were far from rare were never or hardly ever sent to any of our museums, and that none of the numerous expeditions of later times brought home even a single specimen of *Poterion*. As far as I can judge even the Siboga-expedition is no exception. My request to several people in our colonies in the Malay Archipelago remained unanswered, till last year, when I received a letter from Dr. P. N. VAN KAMPEN, assistant Zool. Mus. Buitenzorg, mentioning, that in his presence three specimens of *Poterion* were dredged off Bantam at a depth of about 25 M. Thus the sponge was found again at last. Dr. VAN KAMPEN was kind enough to send me fragments, well preserved in 96% alcohol; he also told me from time to time when new specimens were collected all from the West part of the Java-sea. We learn from this, that the sponge is not rare.

Since nothing was known about the anatomy of the "soft parts" of *Poterion*, I was rather anxious to study microscopical sections of well-preserved specimens. It struck me at once that the structure of this *Poterion* closely resembles that of the so-called *Osculina polystomella* O. S. of which I prepared a description and drawings many years ago²⁾.

Now this *Osculina* is nothing but the "free form" of a boring sponge, as first pointed out by CARTER³⁾; LENDENFELD afterwards (1895)⁴⁾ proclaimed *O. polystomella* as the free form of *Vioa viridis* O. S. Independently of LENDENFELD I arrived at about the same result.

It was, therefore, but a logical conclusion to suppose that *Poterion patera* was likewise the free stage of a boring sponge, and I begged Dr. VAN KAMPEN to look whether in the localities where *Poterion* was dredged, shells, corals, limestone or similar substances occurred which were attacked by Clionidae. Meanwhile I reexamined the specimens of *Poterion* in the Leyden Museum. The director of the Museum, Dr. F. A. JENTINK was so kind as to allow me to cut

1) Natuurk. Verhandel. Prov. Utr. Gen.

2) MS. for Fauna and Flora of the Bay of Naples. By unforeseen events the publication had to be postponed more than once. I am indeed very glad to be able to say that the bulk of the MS. is ready and I hope that no serious interruptions will prevent me from going to press soon.

3) Ann. d. Mag. Nat. Hist. (4) V.

4) Zool. Anzeig. p. 150.

one specimen across for further examination. This I did with a specimen to which I gave the number 338. At the base of the sponge, which is somewhat broadened, I found between the "roots" much sand, rather large pebbles and a number of shells. One of these is a *Voluta scapha* Gmel. of about 10 cm. \times 5 cm.; it shows on its surface numerous holes of a boring sponge, which has pierced the shell a good deal and which has already destroyed a portion of the surface. Microscopical examination of the dried sponge-substance in the interior of the *Voluta* proved that the spiculation closely resembles that of the *Poterion* 338. The sponge substance on the surface of the shell is continuous with that of the *Poterion*. My supposition that *Poterion* represents the free stage of a boring sponge is hereby proved. I am not yet prepared to say whether it is identical with one of the numerous known species. I hope to be able to settle this later on and to give a full account (with illustrations) of the subject. I shall then discuss why only a small portion of *Voluta* is destroyed and the possible mode of growth. As to the anatomy of the spirit-specimens now at my disposal, a brief account may follow here.

A longitudinal section through the wall of the cup, somewhat nearer its basis than its border, where the wall has a thickness of about 25 mm., shows that the cortex has on both sides about the same thickness, viz. 1—5 mm. The parenchyma shows large incurrent and excurrent canals, both surrounded by a transparent tissue. The main incurrent canals have a diameter of 0.5 mm., the main excurrent canals of 0.5—1 mm.; with the transparent tissue the former are, on an average, 3 mm. the latter 5 mm. Both enter deeply into the parenchyma; the former 15—20 mm., the latter 10—15 mm. In their course through the parenchyma the incurrent canals show several round apertures — the beginnings of secondary canals. The mass between these main canals and the surrounding tissue is composed of a crumb-of-bread like substance, and the trabecular network of the skeleton. At this part of the cup the incurrent apertures, stomions, are situated on the outside. They are congregated into pore-areas of indistinct outline; these areas are nevertheless clearly visible as dark brownish spots on a buff-coloured background. The areas have a diameter of a little more than a millimeter, and are situated at about the same distance from each other. In some places the areas are somewhat sunken; in dry specimens this shrinkage goes a good deal farther. I have not been able to detect the stomions on the surface; but sections clearly show that they are placed more or less in rows which start from a common centre. They are the apertures

of narrow and short canals which open just under the dermis into wider canals of which generally 5—6 unite in a common centre. These canals cause the star-like figures, already described by HARTING. Tangential sections show this plainly; it becomes then obvious that these cortical canals sometimes ramify; but the final result is always that on an average five unite into a common wider canal, at right angles to the surface which runs through the rest of the cortex. It is evident that this latter canal corresponds to the incurrent chone¹⁾ of Tetraxonia, as sections at right angles to the surface prove.

The incurrent chones lead into the main incurrent canals; some of these, as stated above, run more or less straight on for about 15—20 mm. at right angles to the sponge surface; they then bend and run in a direction almost parallel to the sponge-surface. In their course they give off branches, which ramify and terminate between a group of the mastichorions. These are ellipsoidal in shape and open with wide apople into the excurrent canals, the system being eurypylous. A certain number of excurrent canals flow together and finally open into the main canals, mentioned above; they traverse the cortex with excurrent chones, which open by procts on the inner surface of the cup.

The soft tissue, surrounding the main canals, excurrent as well as incurrent, is very remarkable. I found the same sort of tissue in many sponges, but especially well developed in the so-called *Osculina polystomella*. LENDENFELD has seen this tissue, and in his description of "*Papillella suberea*" says²⁾: "Das hyaline Gewebe, welches die Hauptkanäle umgibt besteht aus einer glashellen Grundsubstanz, in welcher zahlreiche multipolare und auch bipolare Zellen liegen, deren lange und schlanke, verzweigte Ausläufer überall mit

¹⁾ Of course I use here the term chone in the sense of SOLLAS, and not in the sense of LENDENFELD. This latter author is entirely wrong in using chone as a synonym for sphincter. SOLLAS wrote in 1880 (Ann. & Mag. Nat. Hist. (5) v. p. 135): "The cortex is traversed by the intermaginal cavities of Bowerbank, or, as I shall term them, the "cortical funnels" or "chonae". They consist essentially of a tube divided by a sphincter into a shorter proximal and a longer distal part, the "ectochone" and "endochone" respectively". Apart from the evident lapsus that in this sentence the words ecto- and endochone stand in the wrong place SOLLAS's meaning is plain enough and this definition is generally accepted. However LENDENFELD has another opinion. Thus, for instance, he writes in 1897 (Die Clavulina der Adria, p. 102—103): "In halber Höhe der Rinde vereinigen sich diese Sammelkanäle zu vertikalen Stammkanälen" And further: "Oben gauz dünn, verdickt sich diese schlauchförmige Einfassung des Stammkanales nach unten hin sehr beträchtlich und bildet proximal, in der Umgebung der erwähnten Verengung, mächtig verdickt einen starken Splincter, der als eine Chone aufzufassen ist". I do not wish to discuss the matter here at length. The quoted passages leave no room for misunderstanding.

²⁾ Clavulina der Adria p. 104—105.

einander anostomosiren, so dass hier ein engmasschiges, spongiöses Netz zu Stande kommt. In einigen der Knotenpunkte dieses Fadennetzes liegen die Zelleiber mit ihrem kugligen Kern, in anderen trifft man nur unbedeutende Plasmaanhäufungen an." In my MS. description of this tissue in Clionidae I differ somewhat from LENDENFELD's interpretation; in *Poterion* I find the same sort of tissue, only still more pronounced. The fact is that the reticulum is by no means simply formed by a network of "Ausläufer" of cells, as it becomes clear by careful focussing that a number of the supposed thread-like processus are really membranes. In *Poterion* these membranes are sometimes of enormous size, even larger than in *Cliona* (*Osculina*). The tissue has a close resemblance to the so-called lymphoid or reticular tissue, as RANVIER and PEKELHARING conceive it.

As to the skeleton of *Poterion*, this is formed by a trabecular very firm network of bundles of closely packed tylostyles. I found in *Osculina* that in some portions of the skeleton the spicula were united by a little spongin. The same holds true for *Poterion*. This is, however, only the case in the centre of the pillars or trabeculae; there is a mantle of spicules at the periphery which is devoid of spongin. The spicula of *Poterion* are tylostyles; the spicule for which I proposed¹⁾ the name spinispira I did not find in the specimens of *Poterion* I examined. We know, however, that in the genus *Cliona* itself spinispirae are often very rare or absent, especially in the so-called free stage. I am of opinion that *Papillina suberea* O.S. is identical not only with *Osculina polystomella* O.S., but also with *Papillina nigricans* O.S. and *Vioa viridis* O.S. They are all nothing but modifications of the very variable *Cliona celata*, as I hope to prove in my "Sponges of Naples". LENDENFELD (1897 l.c. p. 99) considers *Papillina suberea* O.S. as a species different from *Papillina nigricans* O.S. This is especially on account of the absence of spinispirae in the former, in a type-specimen of which LENDENFELD failed to find them. I found, however, in the collection of the Zoological Station at Naples a sponge labelled by SCHMIDT *P. suberea*; in this specimen I did find spinispirae. I found them likewise in some of the specimens I collected near Trieste. For these reasons I cannot distinguish *nigricans* from *suberea*. Consequently there is in the absence of spinispirae in *Poterion* no ground for not placing this sponge in the same group as *Cliona*, since in every respect the anatomical structure of *Poterion* resembles that of *Osculina*.

Leyden, May 14, 1908.

¹⁾ On the shape of some Siliceous Spicules of Sponges. (Kon. Akad. v. Wetensch. Amsterdam, 1902. Proceedings p. 104—114).

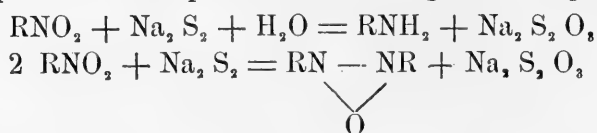
Chemistry. — “*Reduction of aromatic nitro-compounds by sodium disulphide.*” By Dr. J. J. BLANKSMA, (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of May 30, 1908).

I have pointed out previously ¹⁾ that sodium disulphide may act on aromatic nitro-compounds in two different ways, namely by substitution or by reduction.

1. Substitution occurs when halogen atoms or nitro-groups are present which under the influence of *ortho*- or *para*-placed nitro-groups have become moveable. These on being treated with sodium disulphide are readily replaced by S₂ and the disulphides thus formed may be converted by oxidation into sulphonic acids. A fairly large number of these cases have been communicated previously ¹⁾.

2. Reduction takes place when the nitro-compounds do not contain any moveable halogen atoms or nitro-groups; a nitro-group is then reduced to an amido-group, whilst generally a small quantity of azo-oxycompound is also produced according to the equations:



A preliminary investigation had shown me previously that alcoholic solutions of nitrobenzene and *o*-nitrotoluene are readily converted by Na₂S₂ into aniline and *o*-toluidine, the Na₂S₂ being oxidised to Na₂S₂O₃. *m*-Dinitrobenzene and *p*-dinitrobenzene when treated with Na₂S₂ yielded, respectively, *m*-diinitroazo-oxybenzene and *p*-dinitroazo-benzene. It was then ²⁾ our intention to further investigate the reducing action of Na₂S₂.

Meanwhile, however, a patent has been granted to KUNZ ³⁾ for the reduction of aromatic nitro-derivatives to amido-derivatives by means of sodium disulphide in aqueous solution and afterwards sodium disulphide has been used by BRAND ⁴⁾ as a partial reducing agent.

I have now studied the reduction of aromatic nitro-compounds by Na₂S₂ in alcoholic solution in a number of cases. The reduction is carried out as follows:

Six grams of nitrobenzene are added to a boiling solution of 12 grams of crystallised sodium sulphide and 1.6 gram of sulphur in

¹⁾ Dissertation. Amsterdam 1900; Rec. 21, 121, 141.

²⁾ These Proc. 1900, (Oct.)

³⁾ Chem. Centr. 1903 II 813.

⁴⁾ Journ. f. pract Chem. 1906. (2) 74, 499.

300 cc. of 96 % alcohol. After boiling for 6 hours, the alcohol is recovered by distillation and the aniline which still contains a little nitrobenzene is distilled in a current of steam. It is then converted into the hydrochloride to separate it from the admixed nitrobenzene; about 5 grams of aniline hydrochloride are obtained. In the same manner were treated *o-m-* and *p-*nitroanisol, *m-chloro-* and bromo-nitrobenzene and dichloro- and dibromonitrobenzene 1. 3. 5. from which were readily obtained the corresponding amido-derivatives to the extent of about 70 % of the theoretical quantity.

In the case of *ortho-* and *para-chloro*nitrobenzene where the halogen atom is replaced by S₂ a simultaneous reduction takes place to a slight extent with formation of *o-* and *p-chloro*aniline.

Ortho- and *m-nitro*toluene readily yield *ortho-* and *meta-*toluidine; with *para-nitro*toluene a secondary reaction occurs, *p-amido*benzaldehyde being formed as well as *p-toluidine*¹⁾.

Besides the above mentioned mononitro-compounds a few dinitro-compounds were subjected to a partial reduction. From sym-dinitro-toluene we readily obtain by means of alcoholic Na₂S₂ 3-nitro-5-amidotoluene; sym-dinitroanisol yields 3-nitro-5-amidoanisol; from 2-4-dinitroanisol (or phenetol) is obtained 2-amido-4-nitroanisol (or phenetol) whilst sym. trinitrobenzene yields 3-5-dinitraniline. A small quantity of the azo-oxycompounds is generally formed in addition to the amido-derivatives. I will also point out that in the reduction with Na₂S₂ the formation of chlorinated byproducts, which are often generated in the reduction of aromatic nitro-compound with Sn and HCl, is avoided. The fact that sodium disulphide may be weighed also gives it an advantage over ammonium sulphide as a reducing agent.

From the above facts it is obvious that an alcoholic solution of Na₂S₂ may be used as a convenient reducing agent.

Physiology. — “*About the determination of hardness in muscles.*”
By A. K. M. NOYONS, Assistant in the Physiological Laboratory
at Utrecht. (Communicated by Prof. H. ZWAARDEMAKER.)

(Communicated in the meeting of May 30, 1908).

At an inquiry into the causes and qualities of the autotonus it struck me how a muscle seemed to become harder, as its autotonus increased. Hitherto the hardness of a muscle was always estimatively determined by digital touching. The above mentioned fact caused

¹⁾ Chem. Centr. 1900. I. 1084. I hope to communicate more analogous cases of intramolecular oxidation later on.

me to look for means of expressing such changes in hardness more accurately in measure and number, as an approximate determination would not do here.

A communication by J. VON UEXKÜLL¹⁾ on the 18th of April last "Die Verdichtung der Muskeln", led me to a separate description of my investigations about the determination of hardness in muscles. In this communication he says: "wir besitzen zwar kein geeignetes Instrument, um das Hartwerden der Muskeln zu messen", while he winds up as follows: "Ich habe geglaubt, auf diese wichtige, aber allzusehr vernachlässigte Eigenschaft der Muskeln hinzuweisen, in der Hoffnung, dass sich jemand findet der einen brauchbaren Apparat konstruiert, um die Muskelverdichtung unabhängig von der Muskelverdickung zu registrieren."

For many decades together mineralogists have made determination of the hardness of materials, in which a number of methods were employed, which, however, in that form could not be applied to living objects. The literature only gathers for what is called hardness in general, data, for which I refer to some authors²⁾ in behalf of those who wish to become more thoroughly acquainted with the subject.

Hardness is a collective idea, including and typifying an amount of qualities: cohesion, elasticity, plasticity, gliding, splitting and fracture. It is on the value which in a concrete case is assigned more especially to one of the qualities mentioned, that depends the general definition which shall be given of hardness. For living objects gliding, splitting and fracture need not be taken into account. I desist from a more detailed separate description of the three remaining qualities: cohesion, elasticity and plasticity. But if these three qualities are paid attention to, AUERBACH'S³⁾ definition of hardness will no doubt be agreed to: "Härte ist eine Art von Festigkeit, nämlich der Widerstand gegen die Bildung von Unstetigkeiten oder dauernden Deformationen beim Drucke zweier sphärischer Oberflächen gegen einander, und kann Eindringungsfestigkeit genannt werden . . . Sie ist quantitativ durch den Grenzeinheitsdruck im Mittelpunkte der Druckfläche bestimmt."

¹⁾ J. v. UEXKÜLL. Die Verdichtung der Muskeln. Originalmitteilung. Zentralblatt für Physiologie. Bd. XXII N^o. 2.

²⁾ H. ROSEBUSCH und E. A. WÜLFING. Physiographie Allgemeiner Teil. Stuttgart 1904.

G. TSCHERMAK. Lehrbuch der Mineralogie. Wien 1905.

EGON MÜLLER. Ueber Härtebestimmung Inaug. Dissert. Jena 1906.

³⁾ F. AUERBACH. Kanon der Physik pag. 119. Leipzig 1899.

The determination of hardness may give absolute and relative values. Among the methods of relative determination that of THOULET¹⁾ appeared to be useful also to determine the relative hardness of living objects.

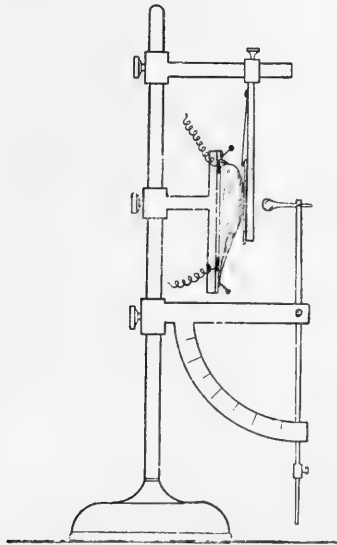
THOULET examined the elasticity of rocks and found points of comparison for this in the number of reflections and in the angle of reflection of a swinging ball suspended in the air. Indeed, if we drop a hard, elastic object upon an other, it will among others depend on the hardness of the surface that is hit, how often and how far the reflection will take place. Now, if this principle is put into practice with a much weaker object like a muscle, these reflections will, though in a smaller degree, yet take place in the same manner, which is corroborated by experience.

The angle of reflection of a falling globule resp. the number of its perceptible taps or reflections depends:

1. on the cohesion, elasticity and plasticity of the falling globule.
2. on the cohesion, elasticity and plasticity of the object hit, in this case the muscle.

Now as in case of comparing determinations sub 1 remains constant, sub 2 must be the only changeable, determinative factor.

The investigation takes place as follows with an apparatus that I call physiological sclerometer.



Physiological Sclerometer. Schematic drawing.

Fig. 1.

¹⁾ M. J. THOULET. Recherches sur l'élasticité des minéraux et des roches. Comptes rendues de l'Académie des sciences. Paris. Tome 96. 1883.

A small pendulum with a fixed turning-point, of which the short beam points upwards to a height of 6 cM., bears on the head of that short arm a handled glass-tear, whilst the other longest arm, 15 cM. long, is provided with a small, movable weight, in consequence of which the moment of that lever-beam is variable. By this way the force with which the head of the glass-tear hits the object, can be made variable. In order to enlarge the living force of the falling object, the pendulum may be given different initial amplitudes. On a scale along which the longest lever moves, this height of falling is expressed in degrees.

The muscle to be examined is by means of its two tendons attached to a somewhat rough surface, here a hard cork-plate, to prevent removal of the muscle by the falling, tapping object. It is advisable in this way to determine the hardness of a muscle under isometric conditions, for, when the muscle is examined under isotonic conditions, the data are getting far less trustworthy, as: 1. in shortening the muscle, the point that is to be touched, by not shortening changes its place and can only be found back by marking it beforehand with colouring matter; 2. the weight necessary for the stretching seems to make the differences in hardness smaller.

The number of times that the glass-tear is reflected by the muscle before it is at rest, is determined either acoustically or by means of photography. The photographic registration has this advantage that at the same time the width of the reflections can be followed.

The photographic registration takes place as follows: the light of an arc-lamp of 220 volt and 10 ampère is by a condenser more or less pressed together into a cone of rays having its focus in a diaphragm. This focus in its turn serves as a source of light and procures by means of a biconvex lens the parallel bundle of rays emitted. This bundle reaches the removable slit of a small box which in its opposite side is provided with a cylinder-lens of GARTEN. The light that has entered through the slit, is by the cylinder-lens, which is graduated, nipped together to an horizontal line of light, which falls through another slit into a second larger box on a drum that is in rotatory motion and to which sensitive bromide-paper of Dr. SCHÄFFELN is fixed. The box containing the drum is impenetrable to light by means of light-free axes. This drum is moved on by a clock, as it is used in the telegraphic Morse-apparatus. Between cylinder-lens and the larger box is placed the long beam of the lever of the sclerometer which during its movements removes a silhouette on the sensitive silver-paper.

The following experiment was made: *M. sartorius* of *Rana temporaria* is alternately passed through by an electric current, arising

by a potential difference of 1.4 volt. For this purpose two brass plates serving as electrodes for the current, had been sunk in the cork sub-stratum of the muscle, whilst by means of a commutator the direction of the current can be changed. At the beginning of the experiment the anode is found at the distal tendon; afterwards the current is turned and ends in its original direction. In the subjoined table occur the widths of the first 4 reflections in mM.

Reflection	Anode at the distal tendon		Kathode at the distal tendon				Anode at the distal tendon	
I	52.5mM.	52mM.	54mM.	53 mM.	54mM.	53mM.	50 mM.	50 mM.
II	29.5	29	31	30	31	31	29.5	29
III	21	21	23	22.5	22	22	21.5	21
IV	16	16	18	17	17	17	16	15.5

The following table gives the difference between the *M. sartorius* of *Rana temporaria* through which a galvanic current has passed and another through which it has not passed.

Reflection	Muscle through which no current is passing			Muscle through which a current is passing Anode at the distal tendon			
I	40 mM.	40.5mM.	40.5mM.	45 mM.	43 mM.	43 mM.	43 mM.
II	24.5	25	25	28	26.5	26	27
III	16.5	17	17	18	17.5	17	17.5
IV	11	11	11	12	11.5	11.5	12

That abundant moistening of a muscle with mutually equimolecular salt-solutions, the effect of which on the autotonus is antagonistic, can alter the hardness, appears from what follows, also holding good for the *M. sartorius* of *Rana temporaria*.

Reflec- tion	Moistening with kaliumchloride				Moistening with natriumchloride					Moistening with kaliumchloride			
	mM.	mM.	mM.	mM.	mM.	mM.	mM.	mM.	mM.	mM.	mM.	mM.	mM.
I	48	42.5	41	40.5	40	37	33	38	38	38	38	38	39
II	33	25.5	25.5	26.5	25.5	24.5	22.5	24	23.5	23	22	22	23
III	24	17	16.5	17	16.5	17.5	16.5	16	15	15	14	14.5	14.5
IV	17.5	11	10.5	11.5	12	12.5	12	10	10	9.5	9	9	9.5
V	12.5	8.5	8	8	9	9	9	7.5	8	8	8	8	8
VI	9	7	7.5	7.5	7.5	8	8	7	7	7	7	7	7

For a plain muscle whose fibres are parallel as in the *M. sartorius* of *Rana*, the above method is a rather fit one, though not in all respects. For the shortening of the muscle is accompanied by a thickening, in consequence of which the distance between muscle and glass-tear is somewhat altered. This is not of much importance for the thin *M. sartorius*, but if the experiment is made with muscles like *M. gastrocnemius*, this difference becomes more considerable, so that it ought to be taken into account. Besides the peculiar rounding of the surface of the muscle may somewhat alter the place of tapping, and in the end the glass-tear sometimes slightly sticks to the muscle, when we are tapping with a small load on the longer beam of the lever.

To meet these and similar drawbacks the following alterations were made. Between muscle and tapping glass-tear is inserted a thin glass plate, which intercepts the taps and transfers them to the muscle. In these circumstances the angle of reflection resp. the number of collisions depends on:

1. the cohesion, elasticity, plasticity of the tapping glass-tear;
2. the cohesion, elasticity, plasticity of the inserted glass plate;
3. the cohesion, elasticity, plasticity of the object to be examined.

Sub 1 and 2 remaining constant, only sub 3 is variable.

In order to come to a determination, the following technical precautions ought to be taken into consideration. The glass plate, a covering glass, is hanging, slightly movable, on a couple of rather stiff horse-hairs. Now the muscle presses this glass plate against an immovable metal fork, so that the glass plate can only make movements in one direction, viz. in the direction of the muscle, as soon as the glass plate is hit by the tapping glass-tear. At every touch of the covering glass the glass globule produces a clearly audible tap. The number of taps is easy to count and is a pretty accurate measure for the number of real movements of the glass, without agreeing with it in number. In proportion as the covering glass is pressed more against the fork by a harder mass of muscles, the oscillations of the little lever will retain a longer and wider amplitude and will also occur more frequently.

The height of falling is of great importance for the effect that is to be reached, in the first place with respect to the number and amplitude of the oscillations.

When at different heights of falling the number of corresponding audible taps is counted for the same muscle, the latter may be represented by a curve, in which the ordinate renders the number of audible taps and the abscis the height of falling in degrees. The curve thus got shows a peculiar course.

No. of the experiment and culture time	Com per cultu on- in salt	Observations
1 24 Febr.—10 April	4 gr. 0,05 K cM ³ . t	
2 26 Febr.—4 April	2 gr. of K ² H P tapwa	
3 13 March—4 April	2 gr. of K ² H P tapwa	
4 26 March—29 April	12 gr. of K ² H P tapwa	
5 6 April—23 April	4 gr. of K ² H P tapwa	Microscop visible infection
6 4 April—29 April	4 gr. of K ² H P tapwa	Microscop. visible infection
7 7 April—2 May	4 gr. of K ² H P tapwa	No microsc. visible infection
8 13 May—29 May	2 gr. of K ² K tapwa	Microcosp. and bac- teriologically pure
9 6 April—23 April	4 gr. of 0,05 K cM ³ . t of cha	
10 16 March—29 April	1 gr. of 0,05 K cM ³ . t	
11 16 March—8 May	1 gr. of nate, () 100 cl	

No. of the experiment and culture time	Components of culture medium in grams.	Inoculation-material	Produced calcium-carbonate in grams	Volatile acid in grams	Totally disappeared limesalt in grams	Nitrogen found after KJELDAHL in milligrams	Nitrogen fixed per gram of decomposed calciumsalt	Observations
24 Febr.—10 April	4 gr. of Calc. Mal. 0.05 K ² HPO ₄ , 200 cM ³ tapwater.	1 st re-inoculation of crude culture in canalwater in same liquid	1.57	0.403	3.3	8.1	2.5	
26 Febr.—4 April	2 gr. of Calc. Mal. K ² HPO ₄ , 200 cM ³ tapwater.	2 ^d transferring of the preceding.			2	5.2	2.6	
13 March—4 April	2 gr. of Calc. Mal. K ² HPO ₄ , 100 cM ³ tapwater.	3 ^d transferring of the preceding	0.872					
26 March—29 April	12 gr. of Calc. Mal. K ² HPO ₄ , 200 cM ³ tapwater.	4 th transferring of the preceding.	5.7	0.632	10.7	18.1	1.8	
6 April—23 April	4 gr. of Calc. Mal. K ² HPO ₄ , 100 cM ³ tapwater.	Pure culture of <i>Azotobacter</i>	0.552	0.112	1.1	1.6	1.5	Microscop visible infection
1 April—29 April	4 gr. of Calc. Mal. K ² HPO ₄ , 100 cM ³ tapwater.	Pure culture of <i>Azotobacter</i>			2.2	5.9	1.7	Microscop visible infection
7 April—2 May	4 gr. of Calc. Mal. K ² HPO ₄ , 100 cM ³ tapwater	Pure culture of <i>Azotobacter</i>	0.494	0.042	0.89	1.5	1.7	No microsc. visible infection
13 May—29 May	2 gr. of Calc. Mal. K ² HPO ₄ , 100 cM ³ tapwater.	Pure culture of <i>Azotobacter</i>	0.8103	0.036	1.39	2.49	1.8	Microscop. and bacteriologically pure
6 April—23 April	4 gr. of Calc. Lactate 0.05 K ² HPO ₄ , 100 cM ³ tapwater, 1 gr. of chalk.	Crude culture from I.		0.101		1.8	1.8	
16 March—29 April	1 gr. of Calc. Acetate, 0.05 K ² HPO ₄ , 100 cM ³ tapwater.	Crude culture from I.	0.576		1	2.8	2.8	
16 March—8 May	1 gr. of Calc. Propionate, 0.05 K ² HPO ₄ , 100 cM ³ tapwater.	Crude culture.	0.491		1	4.7	4.7	

The above experiment was made with a dead muscle, to avoid as much as possible all variable factors of the living object. These come into operation, as appeared from experiments, in which first a curve was produced by observations of a living muscle, and the next day a second curve could be formed from observations of the now dead muscle, which under a glass cover with saturated vapour of water and thymol-vapour was preserved resp. from desiccating and rotting. The values denoted by the curve are averages got from at least five observations each time, which did not materially differ from each other.

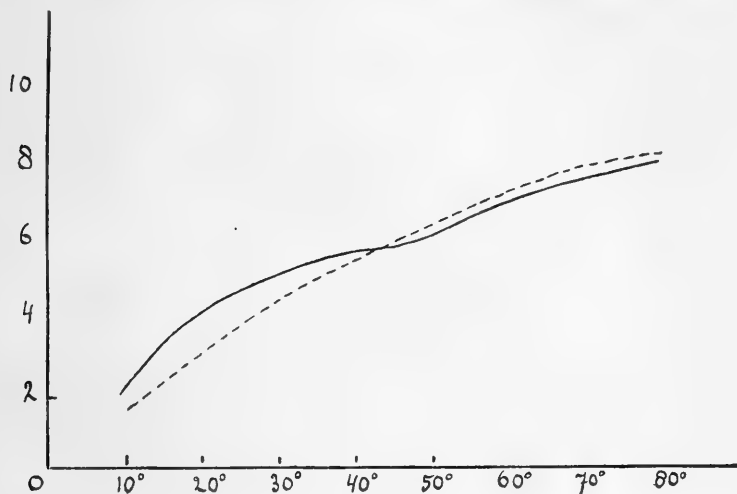


Fig. 2.

Hardness with regard to different heights of falling by a muscle in its dead and living situation.

— = living muscle. - - - - - = dead muscle.

The ordinate gives the number of audible taps and the abscis the initial height of falling in degrees.

In different ways the hardness of a muscle can be made to undergo changes, which are either permanent, or which exist long enough for the determining investigation :

1. by making a galvanic current pass through a muscle;
2. by abundant moistening with equimolecular salt-solutions;
3. by faradaic excitement, either direct or indirect, so that the muscle is in tetanus;
4. by heating, resp. cooling.

An example of the two first mentioned manners was given before; one of the two other manners is as follows: a muscle is by indirect excitement with a faradaic current alternately brought to tetanus. At corresponding moments the determinations of hardness take place.

The subjoined table contains the width of the first 8 reflections which were reproduced photographically; at the same time the duration of these 8 reflections was calculated.

M. gastrocnemius of *Rana temporaria*.

	Normal muscle	Excited to tetanus	Not excited	Excited to tetanus	Not excited	Excited after rest
I	56 mM.	61 mM.	56 mM.	57 mM.	56 mM.	59 mM.
II	38	45	39	43	40	44.5
III	29	35	29	33	31	33
IV	22	28	22.5	26	23.5	26
V	17	22.5	17.5	21	18	21.5
VI	13	18.5	13	16.5	14	17
VII	11	15.5	11.5	13.5	12	13.5
VIII	9.5	12.5	10	11.5	10	11.5
Duration of the first eight reflections.						
	4.4 sec.	4 sec.	4.3 sec.	4 sec.	4.3 sec.	4 sec.

From this it appears that in comparing the first 8 reflections not only the amplitude changes, but that also the time in which these oscillations take place, varies with the greater or smaller degree of hardness of the muscle. As the experiment progresses, it may be observed in the table that the heights of the reflections are getting larger also at the moments when the muscle is not excited. This must be connected with the changes in the constant state of contraction (autotonus), which arise in every fatigued muscle. That the muscle becomes really tired, is proved by the fact: 1. that the muscle visibly contracts less, 2. that changes in duration and height of the reflections diminish after repeated excitement, 3. that after the rest the effect of excitement agrees again with what was observed in the beginning of the experiment.

We add a tabulated statement of an experiment in which the muscle at the end of the experiment had become entirely inexcitable, as appeared from the absence of visible contractions, both for indirect and direct faradaic excitement, though still slight alterations in hardness appeared to be perceptible.

M. gastrocnemius of *Rana temporaria*
becoming inexcitable according to every-day parlance.

	Normal muscle	Excited	Not excited	Excited	Not excited	Excited
I	53 mM.	60 mM.	48 mM.	52 mM.	48 mM.	50 mM.
II	40	50	35	38	35	36
III	28	36	24.5	26	24.5	26.5
IV	21	27	17.5	18	17.5	19
V	15	21.5	13	14	13	15
VI	12.5	17	12	12.5	12	12.5
VII	10.5	13.5	11	11	11	11.5
VIII	10	11.5	10	10	10	10
Total duration of the first 8 reflections.						
	5.4 sec.	5.2 sec.	5.2 sec.	5 sec.	4.4 sec.	4.8 sec.

M. gastrocnemius of *Rana temporaria*.

	Temperature in temperator			
	12.5° Celsius		56° Celsius	
I	49 mM.	49 mM.	50 mM.	50 mM.
II	38	39	41	41
III	27	27.5	31	30.5
IV	19.5	20	25	24.5
V	16	16	21	21
VI	13.5	14	18	18
VII	13	13	16	16
VIII	12	12.5	14.5	14.5
Audible taps				
	7	7	10	10
Total duration of the first 8 reflections in abscis-length				
	3.6 cM.	3.8 cM.	3.2 cM.	3 cM.

If a striated muscle is heated, it shortens: this is accompanied, as appears from the experiments, by changes of hardness. In order to trace this, the muscle in the sclerometer, instead of to a corkplate, was fixed to the thin copper bottom of a temperator, now serving as resting-surface. Through this temperator, as THUNBERG pointed out for the examination of the cold- and heat-points of the skin, alternately cold and hot water could be made to circulate. The copper bottom communicates the heat to the muscle; the temperature in the temperator and that which the muscle gets, will not soon be the same, but still is always in close connection with it.

As a demonstration I give here a couple of photographic reproductions of the oscillations of the beam of the sclerometer, as they were made, and from which among others the above table was partly derived. Fig. 3 gives the sclerometric reproduction of hardness of a muscle at a temperature of 12.5° C. in the temperator, whilst fig. 4 shows the reproduction when the same muscle is heated to 56° C. (See figs 3 and 4).

If a muscle is heated to not too high a temperature, a decrease of hardness manifests itself again after cooling, even though the muscle does not quite reach its original degree of hardness.

The subjoined table makes this clear.

M. gastrocnemius of *Rana temporaria*.

	Temperature in temperator						
	13° Celsius		61° Celsius			11° Celsius	
I	49 mM.	49 mM.	50 mM.	50 mM.	50 mM.	49 mM.	49 mM.
II	37	38	42	41	41	38	39
II	28	30	34	33	33	30	30
V	24	24.5	29	28	28	25	25
V	20	20	25	25	24	21.5	22
VI	17	17.5	22	22	21.5	18.5	19
VII	14	15	20	19.5	19	16.5	17
VIII	12.5	12.5	18	17.5	17.5	14.5	15
	Audible taps						
	10	10	15	16	16	13	13

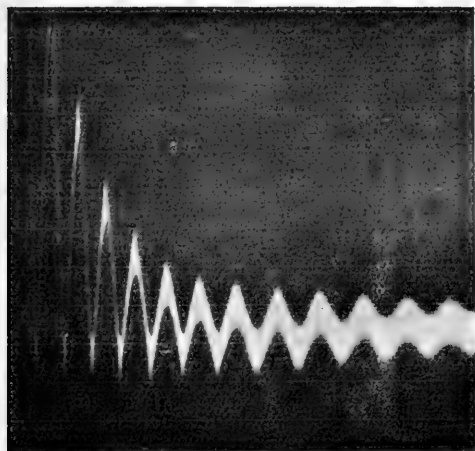


Fig. 3.

Sclerometric reproduction of hardness :
at 12,5° Celsius.

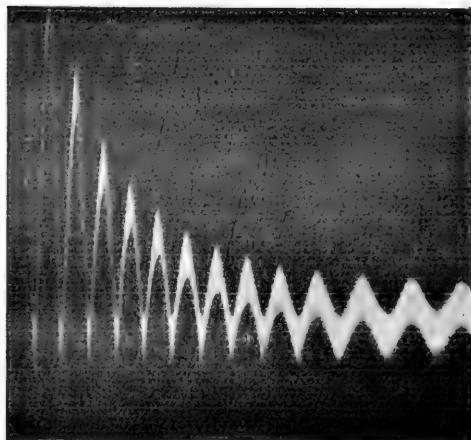


Fig 4.

at 56° Celsius.



Such warming and cooling can be repeated a couple of times, whilst in proportion to this the number of reflections continues varying, provided the muscle be not for too long a time exposed to too high a temperature, as in this case a clearly perceptible permanent hardness will show itself.

Physiology. — “*On the structure of the ganglion-cells in the central nervous system of Branchiostoma lanc.*” (Second communic.)

By Dr. J. BOEKE. (Communicated by Prof. G. C. J. VOSMAER).

(Communicated in the Meeting of May 31, 1908).

a. *The infundibular organ.*

The cells of the differentiated part of the ventral cerebral wall of Branchiostoma, which I described some years ago in these Proceedings¹⁾, and which was then called the *infundibular organ* on account of its place and the homology that could be drawn from that, are quite different in their structure from the other cells, of which I gave a description in my former paper²⁾.

Among the authors, who in recent years have published researches on the central nervous system of amphioxus, KUPFFER³⁾ gives the same description of the cells as I gave in my paper in 1902, and only mentions the organ as consisting of long cylindrical cells with curved cilia and a clear hyaline protoplasm. KUPFFER homologises the differentiated epithelium with the tuberculum posterius of the craniote embryos. JOSEPH⁴⁾ only mentions the organ without adding anything to the description. EDINGER⁵⁾ who examined preparations stained after the method of BIELSCHOWSKY, calls it “das aus grossen Flimmer- und Sinneszellen bestehende Infundibularorgan”, without mentioning on what is founded the opinion, that there are two kinds of cells to be found. In the drawings reproduced in his paper nothing is to be seen but a faint striation of the ventral wall of the brain at the place of the infundibular organ. According to WOLFF⁶⁾ there is a striking resemblance between the differentiated epithelium of the infundibular organ and the gelatinous tissue that we find in the

1) Proc. Roy. Acad. of Sc. of Amsterdam, Math. Phys. Cl. Meeting of April '07 p. 86.

2) Proc. Roy. Acad. of Sc. of Amsterdam, Math. Phys. Cl. Meeting of April '02 p. 695.

3) Handbuch der Entwicklungslehre (HERTWIG), Vol. 2, 3d part.

4) Verhandl. d. Anat. Gesellsch. 18. Vers. 1904.

5) Anat. Anzeiger, Bd. 28, 1906.

6) Biol. Centralblatt. Bd. 27, 1907.

central nervous system of the higher vertebrate animals, but evidently he has not seen much of the real structure of the tissue. Besides these statements nothing more is to be found about this part of the brain of amphioxus, and so we seem to be justified in giving an exact description of it here.

To do this it is necessary to study first of all very thin carefully orientated median sections, as well as frontal and cross sections; the statements by EDINGER made it necessary to examine a great many BIELSCHOWSKY-preparations to form a correct opinion in this matter; hence we took so long for our research.

From the very early period at which the infundibular organ is regularly found and the constancy with which it appears, always in exactly the same form and structure, it is evident that it must play a distinct and important part in the animal's life. Already in larvae with only three primary gill clefts the differentiated epithelium is very obvious. Just where the narrow central canal opens into the wider part of the brain-ventricle, we see the ventral limit of the central canal rise slightly and sink again to the former niveau immediately after. This elevation is caused by the cells in the ventral wall growing out into long cylindrical elements, each cell bearing a long hair or cilium curving backwards, the cells lying regularly one beside the other.

It is an important feature in the development of the infundibular organ that the elongation of the cells first shows itself not in the median line but at the left side of the median plane; afterwards the cylindrical cells are also found at the right side. It is only at a much later stage that the long cells fuse in the median line and become one single mass. This and peculiarities in the course of the nerve-fibres springing from the cells in the full-grown organ, point to a bilateral origin of it.

The cylindrical elongation of the cells is the only change we find. There is no indentation at all of the wall of the brain in front of the organ to be found.

Already in very young animals we see in well-preserved and well-stained preparations that the cilia of the long cells point backward with a slight curve, the cilia of all the surrounding cells pointing forward, to the anterior neuroporus.

In older specimens we find the same state of things, but the cells get still more elongated, and the nucleus, now being small and spherical, is lying near the basis of the cell. All cells are directed backwards, that is to say, their free surface being turned craniad. (fig. 8).

For the topographical relations of the differentiated epithelium to

the other parts of the brain I refer to my former paper (1902).

I can only state here in reference to the contradictory statement of EDINGER, that even in more developed and in full-grown specimens I never found another kind of cells in the organ nor an indentation of the brainwall in front of the infundibular organ (KUPFFER). In fig. 1 is drawn a median section of the full-grown organ, and here we see that the cells are not slanting any more, but are directed perpendicularly to the longitudinal axis of the body. In slightly younger animals one often finds the greater part of the cell still curved backward, while the upper part of the cell has assumed the perpendicular direction already (fig. 4*a*). The cause of this change must be sought in the different rate of growth of the surrounding tissue, the whole cerebrum becoming shorter, and changing from an oblong into a more rounded form.

As I mentioned before, the cells of the infundibular organ have all a backwards curved cilium; these cilia form a plume reaching to the narrow part of the central canal. In young animals being examined alive under the microscope the transparent tissue all round the brain ventricle allows the course of these cilia to be very clearly visible, and then the cilia of all the surrounding cells, pointing forward to the anterior neuroporus, appear as straight hairs forming a compact bundle which runs towards the neuropore, into which the hairs can be traced as long as it is open. The back end of this bundle of cilia is crossed by the cilia of the infundibular-cells:

The form of the cells in the full-grown animal is shown in fig. 4*b*. The neurofibrillar differentiation in the protoplasm of the cell, as I described it already in my former paper, the neurofibrillar network round the nucleus and the way, in which the neurofibrilla leaves the cell is in Fig. 3 clearly to be seen. The course of the nerve-fibres after they left the cell-body I could not trace much farther with a sufficient amount of certainty. They all seem to curve backwards (caudal), and from the study of frontal sections it was possible to draw the conclusion that the nerve-fibres springing from the cells form two bundles, each at one side of the median plane, running backwards, but getting lost to view between the other fibres of the medulla very soon after.

I never succeeded in finding an indentation of the ventral cerebral wall in front of the infundibular organ, as described by KUPFFER, although a large number of serial sections were examined. It is true, that, as I mentioned before, often the nuclei in the ventral wall in front of and behind the differentiated epithelium lie closer together than in the other regions and in a few cases the arrangement of

these nuclei made the impression of a solid indentation. But upon closer examination I always found that this was only an apparent and no real indentation (infundibulum). Here one must be very careful not to draw any conclusions from a few series of sections. In a median section through the infundibular organ from one of my longitudinal series of a 47 mm. long Branchiostoma one would be inclined to draw the conclusion that there exists a groove-shaped indentation of the brainwall behind the organ, no trace of any indentation being found in front of it. So I think it dangerous to found a homology on this indentation, as KUPFFER did, and I adhere to the denomination "infundibular organ", as its structure and development have more resemblance with the epithelium in the saccus vasculosus of the ichthyopsidae, to which I gave the same name, than with the tuberculum posterius, which is still somewhat problematical.

b. *Shape and development of the brain-ventricle.*

I will here only mention those facts that are important for the comparison between the Branchiostoma cerebrum and that of the craniotes, and for the question whether the differentiated epithelium mentioned above may be homologised with the infundibular epithelium, or with the tuberculum posterius.

The second homology might be concluded from the drawing published by KUPFFER in 1894 and 1903, representing a median section through the cerebrum of a 2 c.m. long amphioxus. But this drawing seems to me not to represent the real state of things. Neither exactly orientated median sections (fig. 8) nor the median sections reconstructed from series of cross-sections (fig. 7) ever gave me anything like this drawing.

And yet it is in this case that the reconstruction-method must give an absolutely certain result. By this method we are able to correct entirely the deviations of the cerebral axis from the longitudinal axis of the body as they are found in almost every specimen. And as the cerebral vesicle has such a simple uncomplicated form this method gives us in every case an exact reproduction of the median section (which is certainly of the high value for the comparison of the brain KUPFFER ascribes to it), and at the same time allows us to get a sure knowledge of the width of the cerebral cavity. I give here three drawings of the median sections reconstructed from the cross-sections, one of a very young larva of 3,4 m.m. (fig. 5), one of a young amphioxus of 10 m.m. (fig. 6) and another of a specimen 21 m.m. long (fig. 7). All these are

reconstructed from cross-sections of 5μ , magnified 800 to 1600 times, and afterwards reduced by means of photography. To fig. 5 I added the cross-sections lying on the spots indicated with *a*, *b*, *c*, *d*, to show the width and form of the cavity at the different spots. In fig. 8 I give the reproduction of a real median section through the brain of a specimen of about the same age as the one the reconstruction of which is given in fig. 7, to show how much they are like each other.

The reconstruction of fig. 5 shows, that even in very young larvae, (larvae of 1.5 to 2 m.m. give about the same picture), in which the brain is still larger in diameter than the spinal cord, there exists a dorsal dilatation of the cerebral cavity, which may be compared with the fourth ventricle of craniote embryos (fig. 5, 6, *VQ*). It represents a dorsal dilatation of the central canal (fig. 5*c*) and is connected with the anterior vesicle by a narrow part (fig. 5*b*). In all my specimens this connection of the ventriculus quartus with the anterior vesicle could be stated with absolute certainty, contrary to the well-known observations by HATSCHEK. Even in very young larvae the connection was very conspicuous. In the caudal part of the dorsal dilatation (fig. 5*d*) the midpart of the narrow fissure-like central canal is obliterated, so that this part of the fourth ventricle is separated from the ventral central canal which remains open. In older animals this obliteration proceeds cranial. The dorsal wall of the fourth ventricle is very thin consisting of one layer of flattened cells, but it is always visible even in very young larvae, if only the specimens are well-preserved.

In much older individuals, which passed through the metamorphosis long ago (fig. 6), the fourth ventricle is still very conspicuous and connected with the anterior vesicle by a narrow dorsal canal. The dorsal wall is still thin and membranous. The large dorsal ganglion-cells (vide my former paper) that are now developed to a certain extent, are still only visible at both sides of the median plane and do therefore not appear in the median section through the brain. Afterwards this peculiar group of cells is developed to such an extent (fig. 7, fig. 8), that they occupy the entire dorsal part of this region of the central nervous system, and so appear also in the median section. It is only then that the distinct fourth ventricle becomes indistinct, irregular, flattened, alters its shape and even disappears here and there. Then we find the peculiar irregular dilatations of the central cavity, described by KUPFFER as "quere Schenkel" and "blasenförmige Erweiterungen". They are not segmental, are only of secondary importance, and are not to be com-

pared with special parts and stages of development of the brain of craniote embryos.

After these statements I will add a few words concerning the cranial or rostral part of the cerebrum and the adjacent organs.

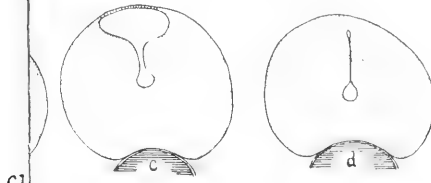
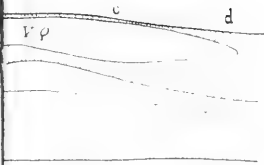
In his paper of 1906 EDINGER describes a new organ, the "frontal organ", lying in front of the brain and being innervated by a special nerve. I regret to say that I (no more than WOLFF in his paper of 1907) could find no trace of a frontal organ. Even after a most careful study of a number of individuals I can only find in the rostrum the often queerly shaped irregular mucous canals (Schleimcanäle) lying ventrally and dorsally of the chorda. They are never connected with the epidermis, but all receive very thin nerve-fibres from the first cerebral nerve.

Although the existence of a distinct nerve connecting the olfactory groove of KÖLLIKER with the brain, is denied by EDINGER, I could find it in my preparations as a bundle of fine nerve-fibres, connecting the sensory cells of the groove with the dorsal part of the brain. In all respects I could affirm the exact observations of DOGIEL (1903)¹⁾ both concerning the sensory cells in the olfactory groove and the nervous connection of them with the brain.

In the dorsal part of the cerebral wall I find a distinct commissural system, wherefrom bundles of nerve-fibres curve backwards (much like the fasciculus retroflexus of the commissura posterior of the craniotes) and a few fibres curve round forward. There are more systems of fibres to be found in the wall of the cerebral vesicle, but they are rudimentary and composed of only a few fibres. This is not the place to enter into details about these things. But when we take all this into account I think it is not permissible to consider the amphioxus-cerebrum as an "archencephalon" (KUPFFER), that has remained on a very low stage of development, but we must regard it as a degenerated cerebral system, which has become rudimentary in many of its parts, a brain which has many of the features of the brain of the ichthyopsides, but there are entirely lacking the organs of the side-line system (lens of the eye, ear, side-line) and because of that and of the fact, that the head has not developed as in the higher vertebrates, it is degenerated and rudimentary. In connection with this and with the elongation of the chorda the foldings of the cerebral vesicle do not appear. Even a plica ventralis does not exist. The infundibular organ remains in the niveau of the ventral cerebral wall.

Leiden. Histological part of the Anat. Kabinet.

¹⁾ Anatomische Hefte 21. Bd. 1903.



Ch
fig. 5.



fig. 6.

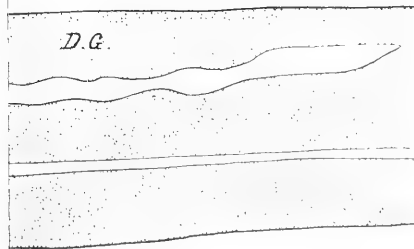


fig. 7.

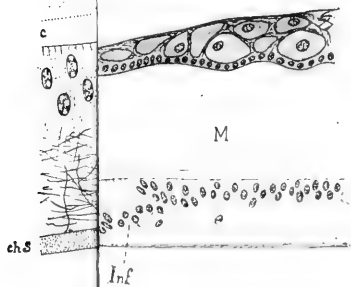


fig. 8.

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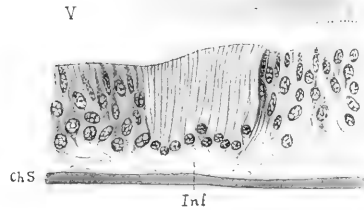


Fig. 1.

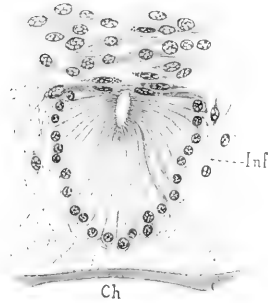


Fig. 2.

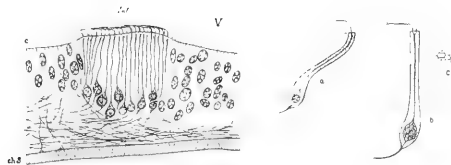


Fig. 3.

Fig. 4.

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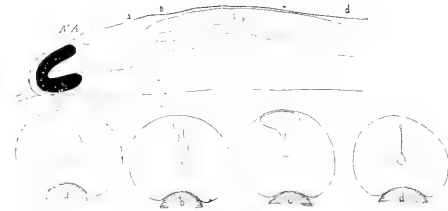


Fig. 5.



Fig. 6.

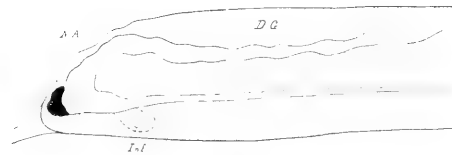


Fig. 7.



Fig. 8.

DESCRIPTION OF FIGURES.

- Fig. 1. Median longitudinal section of the infundibular organ of a Branchiostoma of 52 m.M. in length, 600: 1.
- Fig. 2. Cross-section through the same of a Branchiostoma of 54 m.M. in length, 600: 1.
- Fig. 3. The same as Fig. 1. Neurofibrillae stained with chloride of gold.
- Fig. 4. Cells of the infundibular organ, a of a Branchiostoma of 22 m.M. in length, b of 50 m.M. in length, c cross-section of the upper ends of the cells.
- Fig. 5. Median section of the brain of a Branchiostoma larva of 3,4 m.M., reconstructed from cross-sections.
- Fig. 6. The same of a specimen of 10 m.M. long.
- Fig. 7. The same of a specimen of 21 m.M. long.
- Fig. 8. Median section through the brain of a Branchiostoma of 28 m.M. in length.

Mathematics. — “*About difference quotients and differential quotients*”. By Dr. L. E. J. BROUWER (Communicated by Prof. D. J. KORTEWEG).

(Communicated in the meeting of May 30, 1908).

Different investigations have been made which are very completely summed up in the work of DINI: “Grundlagen für eine Theorie der Functionen einer veränderlichen reellen Grösse” Chapt. XI and XII, on the connection between difference quotients and differential quotients, particularly on the necessary and satisfactory properties which the difference quotients must possess in order that there be a differential quotient. One however always regards in the first place these different difference quotients in one and the same point x_0 together, forming as a function of the increase of x the *derivatory function in x_0* . The existence of a differential quotient means then, that that derivatory function has a single limiting point in x_0 i.o.w. that in x_0 the right- as well as the left *derivatory oscillation* is equal to zero.

Other conditions for the existence of a differential quotient are found when in the first place the difference quotient for constant x -increase Δ is regarded as a function of x and then the set of these functions for varying Δ is investigated. Let $f(x)$ be the given function which we suppose to be finite and continuous and let $\varphi_\Delta(x)$ be the difference quotient for a constant x -increase Δ . The different functions $\varphi_\Delta(x)$ form an infinite set of functions, in which each function is continuous. We shall occupy ourselves with the

case that the set is *uniformly continuous*, i. e. that for any quantity ε , however small it may be, a quantity σ can be pointed out so that in any interval of the size of σ not one of the functions of the set has oscillations larger than ε . Concerning infinite uniformly continuous sets of functions there is a theorem that if they are limited (i.e., if a maximum value and a minimum value can be given between which all functions move) they possess *at least one* continuous limiting curve, to which uniform convergence takes place¹).

We shall prove, that for the set of functions of the difference quotients of a finite continuous function, if it be uniformly continuous, follows in the first place the limitedness and furtheron for indefinite decrease of the x -increase the existence of only *one* limiting curve, so that holds:

Theorem 1. If a finite continuous function $f(x)$ has a uniformly continuous set of difference quotients, then it possesses a finite continuous differential quotient²).

To prove this we call ${}_{\delta}\varepsilon_{\Delta}(x)$ the size of the region of oscillation between x and $x + \Delta$ of the difference quotient for an x -increase δ . If we allow δ to assume successively all positive values, then it follows from the supposed uniform continuity, that Δ can always be chosen so small as to keep all values ${}_{\delta}\varepsilon_{\Delta}(x)$ below a certain amount as small as one cares to make it. If we thus call $\varepsilon_{\Delta}(x)$ the maximum of the values ${}_{\delta}\varepsilon_{\Delta}(x)$ for definite x and Δ , then $\varepsilon_{\Delta}(x)$ tends with Δ uniformly to 0.

We have fartheron if $\frac{p}{n}$ is a proper fraction:

$$\varphi_{\Delta}(x) = \frac{1}{n} \varphi_{\frac{\Delta}{n}}(x) + \frac{1}{n} \varphi_{\frac{\Delta}{n}}\left(x + \frac{1}{n} \Delta\right) + \dots + \frac{1}{n} \varphi_{\frac{\Delta}{n}}\left(x + \frac{n-1}{n} \Delta\right) \quad (1)$$

$$\varphi_{\frac{p}{n}\Delta}(x) = \frac{1}{p} \varphi_{\frac{\Delta}{n}}(x) + \frac{1}{p} \varphi_{\frac{\Delta}{n}}\left(x + \frac{1}{n} \Delta\right) + \dots + \frac{1}{p} \varphi_{\frac{\Delta}{n}}\left(x + \frac{p-1}{n} \Delta\right). \quad (2)$$

If we break up each of the n terms of the second member of (1) into p equal parts and each of the p terms of the second member of (2) into n equal parts, then the difference of those two second members can be divided into pn terms, each remaining in absolute value smaller than $\frac{1}{pn} \cdot \varepsilon_{\Delta}(x)$, so that the difference of $\varphi_{\Delta}(x)$ and $\varphi_{\frac{p}{n}\Delta}(x)$ remains smaller than $\varepsilon_{\Delta}(x)$ in absolute value.

¹) Compare ARZELÀ, "Sulle funzioni di linee", Memorie della Accademia di Bologna, serie 5, V, page 225.

²) We suppose the function to be given in a certain interval of values of the independent variable x .

So if we regard for any definite x all difference quotients the x -increases of which are equal to proper fractions of Δ , then the amount $\tau_{\Delta}(x)$ of their region of oscillation is smaller than $2\varepsilon_{\Delta}(x)$. The same holds for the region of oscillation of *all* difference quotients for definite x with x -increases smaller than Δ , because these can be approximated by the preceding on account of the continuity of f .

So if we allow Δ to decrease indefinitely, then also $\tau_{\Delta}(x)$ decreases indefinitely; as furthermore when Δ becomes smaller, each following region of oscillation is a part of the preceding, the limit of the region of oscillation is for each x a single definite value, to which uniform convergence takes place, which is the limit of the difference quotients, the *differential quotient*.

That this (forward) differential quotient cannot show any discontinuities, is evident as follows: If there were a discontinuity, then there would be a quantity σ which could be overstepped there for any interval by the oscillations of the differential quotient; but if the value of the differential quotient differs in two points more than σ , then there is also a difference quotient the values of which in those two points differ more than σ ; so there would be for each interval, which contains the indicated discontinuity, a difference quotient with a region of oscillation larger than σ , i. o. w. the functional set of the difference quotients would not be uniformly continuous.

Out of the continuity of the forward differential quotient follows at the same time that the forward and the backward differential quotient are equal.

Analogously it is evident that also a point at infinity in the differential quotient would disturb the uniform continuity of the difference quotients; in this is at the same time included the limitedness of the difference quotients, for they would otherwise on account of the finiteness of f be able to tend to infinity only for indefinitely decreasing x -increase, but that would furnish an infinity point in the differential quotient.

Theorem 2. Of a function with finite continuous differential quotient the difference quotients are uniformly continuous.

Let namely ε be a definite quantity, to be taken as small as one likes. Now we may have each x included by an interval i in such a way, that the oscillations of the differential quotient within each of those intervals remain smaller than $\frac{1}{2}\varepsilon$. On account of the uniform convergence, evident from the formula $\varphi_{\Delta}(x) = f'(x + \vartheta\Delta)$, a Δ' can be pointed out in such a way that all φ_{Δ} for which $\Delta < \Delta'$ differ from the differential quotient less than $\frac{1}{4}\varepsilon$ for any x , thus

have their oscillations below ε in the intervals mentioned. On account of the uniform continuity of f we may furthermore have each x included by an interval i' chosen in such a way that for all $\Delta \geq \Delta'$ the corresponding φ_Δ have within those intervals oscillations below ε only; to that end we have but to choose i' in such a way that the oscillations of f remain within the intervals below $\frac{1}{2}\varepsilon\Delta'$. If thus i'' is the smaller of the two quantities i and i' , each x can be included by an interval i'' in such a way, that the oscillations of *all* difference quotients within it remain below ε , with which we have proved the uniform continuity of the difference quotients.

Theorem 3. If there is among the difference quotients of a finite continuous function a uniform continuous fundamental series with indefinitely decreasing x -increases, there exists a finite continuous differential quotient.

Let namely $\varphi_{\Delta'}(x), \varphi_{\Delta''}(x), \dots$ be the fundamental series of functions under consideration, then for any quantity ε we can point out a quantity σ in such a way that $\varphi_{\Delta^{(\nu)}}(x+h) - \varphi_{\Delta^{(\nu)}}(x) < \varepsilon$ for any x , any $h < \sigma$ and any ν . If now the set of *all* difference quotients were not uniformly continuous, it would have to occur that for a certain Δ° not belonging to the fundamental series we should have $\varphi_{\Delta^\circ}(x+h) - \varphi_{\Delta^\circ}(x) > \varepsilon$. If we now approximate Δ° by a series $\alpha_1\Delta', \alpha_2\Delta'', \dots$, where the α 's represent integers, in such a way that $\alpha_p\Delta^{(\nu)} < \Delta^\circ < (\alpha_p+1)\Delta^{(\nu)}$, then also $\varphi_{\Delta^\circ}(x+h) - \varphi_{\Delta^\circ}(x)$ is approximated by $\varphi_{\alpha_p\Delta^{(\nu)}}(x+h) - \varphi_{\alpha_p\Delta^{(\nu)}}(x)$, which last expression always remains $< \varepsilon$ however large p may become, so that $\varphi_{\Delta^\circ}(x+h) - \varphi_{\Delta^\circ}(x)$ cannot be $> \varepsilon$, so the set of *all* difference quotients is uniformly continuous, and there is a finite continuous differential quotient.

Theorem 1 is applied when building up the theory of continuous groups out of the theory of sets, (where one remains independent of LIE's postulates), in a certain region finite and continuous functions of one or more variables occurring there, whose difference quotients are in a certain system of coordinates linear functions of the original functions.¹⁾ As on account of the finiteness of the original functions there cannot be a region within which any quantity could be overstepped everywhere by one and the same difference quotient, the

¹⁾ Comp. L. E. J. BROUWER, "Die Theorie der endlichen kontinuierlichen Gruppen unabhängig von den Axiomen von LIE", Atti del IV^o Congresso Internazionale dei Matematici. It is the differentiability in one and the same system of coordinates of all the functions, which express the different infinitesimal transformations of a group, which is proved in this way.

coefficients of the above mentioned linear functions remain within finite limits, the system of the difference quotients is uniformly continuous, and the differential quotients exist.

Theorem 4. If the conditions of theorem 1 are satisfied and if the system of all second difference quotients (of which each is determined by two independent x -increases) forms a uniformly continuous system, then there exists a finite continuous "second differential quotient" which at the same time is the only limit of the above set of functions when both x -increases decrease indefinitely, and the differential quotient of the (first) differential quotient.

To prove this we call $\varepsilon'_\Delta(x)$ the maximum size of the regions of oscillation of the different second difference quotients between x and $x + \Delta$; then again $\varepsilon'_\Delta(x)$ tends with Δ uniformly to zero.

If we represent the difference quotient of $\varphi_{\Delta_1}(x)$ for an x -increase Δ_2 by $\varphi_{\Delta_1\Delta_2}(x)$ and if $\frac{p_1}{n_1}$ and $\frac{p_2}{n_2}$ are proper fractions then we have:

$$\varphi_{\Delta_1\Delta_2}(x) = \frac{1}{n_1 n_2} \sum_{k_1=0}^{n_1-1} \sum_{k_2=0}^{n_2-1} \varphi_{\frac{\Delta_1}{n_1} \frac{\Delta_2}{n_2}} \left(x + k_1 \frac{\Delta_1}{n_1} + k_2 \frac{\Delta_2}{n_2} \right). \quad (1)$$

$$\varphi_{\frac{p_1\Delta_1}{n_1} \frac{p_2\Delta_2}{n_2}}(x) = \frac{1}{p_1 p_2} \sum_{k_1=0}^{p_1-1} \sum_{k_2=0}^{p_2-1} \varphi_{\frac{\Delta_1}{n_1} \frac{\Delta_2}{n_2}} \left(x + k_1 \frac{\Delta_1}{n_1} + k_2 \frac{\Delta_2}{n_2} \right). \quad (2)$$

If we break up each of the $n_1 n_2$ terms of the second member of (1) into $p_1 p_2$ equal parts and each of the $p_1 p_2$ terms of the second member of (2) into $n_1 n_2$ equal parts, then the difference of those two members breaks up into $p_1 p_2 n_1 n_2$ terms, each of which remaining in absolute value smaller than $\frac{1}{p_1 p_2 n_1 n_2} \varepsilon'_{\Delta_1 + \Delta_2}(x)$, so that the difference of $\varphi_{\Delta_1\Delta_2}(x)$ and $\varphi_{\frac{p_1\Delta_1}{n_1} \frac{p_2\Delta_2}{n_2}}(x)$ remains in absolute value smaller than $\varepsilon'_{\Delta_1 + \Delta_2}(x)$.

So if we consider for any definite x all difference quotients whose x -increases are equal to proper fractions of Δ_1 and Δ_2 , then the size $\tau_{\Delta_1\Delta_2}(x)$ of their region of oscillation is smaller than $2\varepsilon'_{\Delta_1 + \Delta_2}(x)$, from which we deduce as above in the proof of theorem 1 the existence of one single limit, to which the convergence is uniform and which is finite and continuous.

If we now regard the difference quotient with x -increase Δ_2 , on one hand for all φ_Δ 's, whose Δ is smaller than Δ_1 , and on the other hand for the (first) differential quotient, then the former all differ less than $\varepsilon'_{\Delta_1 + \Delta_2}(x)$ from the limiting function just deduced, so also the latter, which can be approximated by them. This holds independently of Δ_1 ;

the difference for x -increase Δ_2 of the (first) differential quotient can therefore not differ more than $\varepsilon'_{\Delta_2}(x)$ from the just deduced limiting function which is thus differential quotient of the (first) differential quotient i.e. second differential quotient.

Theorem 5. If a function possesses a finite continuous second differential quotient, then the system of the first and second difference quotients is uniformly continuous.

To find namely an interval size i'' which keeps the oscillations of all second difference quotients everywhere $< \varepsilon$, we first take the interval size i , which keeps the oscillations of the second differential quotient everywhere $< \frac{1}{2} \varepsilon$; then a Δ'_1 and a Δ'_2 in such a way, that all $\varphi_{\Delta_1 \Delta_2}$, for which $\Delta_1 < \Delta'_1$ and $\Delta_2 < \Delta'_2$, differ along the whole course less than $\frac{1}{4} \varepsilon$ from the second differential quotient¹⁾; finally an interval size i' which keeps the oscillations of the function f everywhere $< \frac{1}{4} \varepsilon \Delta'_1 \Delta'_2$. For i'' we take the smaller of the two quantities i and i' .

Theorem 6. If there is among the second difference quotients of a finite continuous function with finite continuous differential quotient a uniformly continuous fundamental series, in which the two x -increases decrease indefinitely, then there exists a finite continuous second differential quotient.

Let namely $\varphi_{\Delta_1' \Delta_2'}(x), \varphi_{\Delta_1'' \Delta_2''}(x) \dots$ be the indicated fundamental series, then for any quantity ε a quantity σ can be pointed out in such a way, that $\varphi_{\Delta_1^{(v)} \Delta_2^{(v)}}(x+h) - \varphi_{\Delta_1^{(v)} \Delta_2^{(v)}}(x) < \varepsilon$ for any x , any $h < \sigma$ and any v . If now the set of all second difference quotients were not uniformly continuous, then it would be possible for a certain Δ_1° and Δ_2° not belonging to the fundamental series, that $\varphi_{\Delta_1^\circ \Delta_2^\circ}(x+h) - \varphi_{\Delta_1^\circ \Delta_2^\circ}(x) > \varepsilon$. Let us now approximate Δ_1° by means of a series $\alpha_1 \Delta_1', \alpha_2 \Delta_1'', \dots$ and Δ_2° by means of a series $\beta_1 \Delta_2', \beta_2 \Delta_2'', \dots$, where the α 's and β 's represent integers, in such a way that

$$\alpha_p \Delta_1^{(p)} < \Delta_1^\circ < (\alpha_p + 1) \Delta_1^{(p)} \text{ and } \beta_p \Delta_2^{(p)} < \Delta_2^\circ < (\beta_p + 1) \Delta_2^{(p)},$$

¹⁾ The uniform convergence of all difference quotients is evident from that of the difference quotients, for which $\Delta_1 = \Delta_2$ (out of these the other can be approximated in the manner indicated in the proof of theorem 6); the latter is evident by developing the terms of $f(x+2\Delta) - 2f(x+\Delta) + f(x)$ according to TAYLOR'S series, in which we make the second differential quotient form the restterm; the terms preceding this restterm then destroy each other.

then also $\varphi_{\Delta_1 \circ \Delta} (x + h) - \varphi_{\Delta_1 \circ \Delta_2 \circ} (x)$ is approximated by

$$\varphi_{\alpha, \Delta_1^{(p)}, \beta, \Delta_2^{(p)}} (x + h) - \varphi_{\alpha, \Delta_1^{(p)}, \beta, \Delta_2^{(p)}} (x),$$

which last expression remains $< \varepsilon$, however great p may become, so that the first can neither be $> \varepsilon$,; so the set of *all* second difference quotients is uniformly continuous and there is a finite continuous second differential quotient.

Theorem 7. If there is among the second difference quotients of a finite continuous function a uniformly continuous fundamental series, in which both x -increases decrease indefinitely, the function possesses finite and continuous first and second differential quotients.

For, according to the above given proof of theorem 6 the whole system of the second difference quotients proves to be uniformly continuous, and out of the above given proof of theorem 4 this system proves to possess for indefinite decrease of the two x -increases one single finite continuous limiting function $f''(x)$ to which they converge uniformly. Let τ' be the maximum deviation from this limiting function of the second difference quotients, whose x -increases are smaller than Δ'_1 and Δ'_2 , and let us regard the system ζ of all $\varphi_{\Delta}(x)$ whose $\Delta < \Delta'_1$, then all difference quotients with x -increase $< \Delta'_1$ of the system ζ lie between $f''(x) + \tau'$ and $f''(x) - \tau'$, from which may be deduced easily, that the system ζ is uniformly continuous, so that now first according to the proof of theorem 1 a finite continuous first differential quotient exists and then according to the proof of theorem 4 a finite continuous second differential quotient.

Analogous to the preceding are the proofs of the following more general theorems:

Theorem 8. If there is among the n^{th} difference quotients of a finite continuous function a uniformly continuous fundamental series, in which all x -increases decrease indefinitely, then the function possesses finite and continuous first, second, up to the n^{th} differential quotients; each p^{th} differential quotient is here first the only limit for indefinitely decreasing x -increases of the p^{th} difference quotients to which limit a uniform convergence takes place, and then differential quotient of the $(p-1)^{\text{st}}$ differential quotient.

Theorem 9. If a function possesses a finite continuous n^{th} differential

quotient, then the system of the first, second, up to the n^{th} difference quotients is uniformly continuous¹⁾.

Theorem 10. If n_1, n_2, n_3, \dots is an infinite series of increasing integers and if of a finite continuous function the systems of the n_1^{st} , of the n_2^{nd}, \dots difference quotients are uniformly continuous, then the function has all differential quotients and these are all finite and continuous.

Theorem 11. A finite continuous function of several variables, among whose difference quotients of the n^{th} order there is for each kind a uniformly continuous fundamental series in which the increases of the independent variables decrease indefinitely, possesses all differential quotients up to the n^{th} order; these finite and continuous differential quotients are first each other's differential quotients in the manner expressed by their form, where the order of succession of the differentiations proves to be irrelevant, and then each differential quotient is the only limit of the corresponding difference quotients for indefinitely decreasing increases of the independent variables, to which limit a uniform convergence takes place.

Theorem 12. If a function of several variables possesses all kinds of n^{th} differential quotients and if these are finite and continuous, then the system of the 1st, 2nd up to the n^{th} difference quotients is uniformly continuous.²⁾

Finally the observation, that what was treated here leads infinite differentiability back to continuity in a more extensive sense, and in this way may somewhat explain, that for so long all finite continuous functions were supposed to be infinitely differentiable, and may somewhat justify that so many wish to limit themselves in natural science to infinitely differentiable functions.

¹⁾ To prove the uniform convergence of the n^{th} difference quotients for equal independent x -increases we break off just as for theorem 5 the Taylor development at the n^{th} term and we apply the formula:

$$n^a - \binom{1}{n} (n-1)^a + \binom{2}{n} (n-2)^a \dots = 0$$

(n and a integers; $a < n$).

²⁾ To prove the uniform convergence of the n^{th} difference quotients with equal independent increases Δ (these Δ indefinitely decreasing) we develop the elements of such a difference quotient according to TAYLOR'S series, in which we make the n^{th} differential quotients form the restterms. The terms preceding the restterms then fall out and of the restterms one kind converges uniformly to the differential quotient corresponding to the difference quotient considered and the other converge uniformly to zero.

Microbiology. — “*Fixation of free atmospheric nitrogen by Azotobacter in pure culture. Distribution of this bacterium*” By Prof. M. W. BEIJERINCK.

(Communicated in the meeting of May 30, 1908).

When carbon hydrates are used as source of carbon in *Azotobacter* cultures, there existed until now some doubt whether the then occurring fixation of free nitrogen was originally effected by *Azotobacter* itself or by other bacteria found in symbiosis with it, because *Azotobacter* in pure culture with carbon hydrates and free nitrogen only, does not show any considerable development.

For this reason I was formerly of opinion that in such cultures *Bacillus radiobacter*, a species closely allied to the bacteria of the Papilionaceae, and which is never absent in accumulations of *Azotobacter*, would be the real cause of the nitrogen fixation.¹⁾

Continued research, however, rendered this supposition more and more improbable, and the facts which are now to be stated have proved beyond any doubt that the said faculty belongs indeed to *Azotobacter* itself.

These facts have regard to the very peculiar relation between *Azotobacter* and the salts of the organic acids, more in particular to calcium malate.

1. *Calcium malate as source of carbon.*

When into a wide ERLÉNMEYER jar a nutrient liquid is introduced of the composition: 100 tap-water, 2 calcium malate, 0.05 K²HPO⁴, with addition of some 10–20 cM³ canal-water, or as much soil for infection, care being taken that the layer of liquid in the jar be not thicker than 2–5 cM, on cultivation in a thermostat at 30° C., usually after 2 or 3 days²⁾ a floating *Azotobacter* film appears, consisting of strongly motile individuals, and relatively soon obtaining a considerable thickness. Hereby so much calcium carbonate is produced that it forms a closed, floating layer, so to say a cover, on the surface of the liquid.

If some of this film is inoculated into another jar containing the same medium, corresponding phenomena are seen when the culture

1) These proceedings of March 1901. Centr. bl. f. Bact. 2te Äbt. Bd. 9 pg. 1, 1902. Archives Néerl. (2) T. 8 p. 190 and 319, 1903.

2) Especially in spring and autumn these experiments succeed. In summer and winter *Azotobacter* seems sometimes absent in the said quantity of water.

conditions are alike. At first sight already, there can be no doubt but under these circumstances fixation of considerable quantities of nitrogen must take place, and chemical analysis proves that this is really the case.

The microscopic image of the *Azotobacter* growth in the malate commonly shows smaller individuals of greater motility than the formerly described forms which are obtained in the mannite solutions. They keep about the middle between *A. chroococcum* and *A. agilis*, and remind strongly of a variety found in America, which has received the name of *A. vinlandi*. The plate cultures of such a malate accumulation again prove not to be pure but to consist of the usual mixture of non spore-forming species. They are best grown on a medium of the composition: 100 tapwater, 1 calciummalate, 0.05 K^2HPO^4 , 1 to 2 agar, on which the *Azotobacter* colonies become already visible after 12 hours at 30° C., which is not the case with any other species of microbes known to me. As these plates are somewhat cloudy by the produced calciumphosphate and the imperfectly dissolved malate, it is desirable to mix the ingredients in the way as follows. Into a culture tube are first introduced some drops of a neutral, concentrated solution of kaliummalate and herein are dissolved both the calciummalate and the kaliumphosphate, with a little water to dilute, but the smallest quantity possible, as the dissolving power of the kaliummalate is much stronger in the concentrated than in the dilute solution. Then the contents of the tube are mixed with the agar solution.

The malate plates prepared in this way have proved to be better for the growth of *Azotobacter* germs than the mannite and glucose plates, so that of a definite number of germs there develop more colonies on the former than on the latter. Hence it has become possible more exactly to compute the number of individuals of our species present in a sample of soil than after the old method, to which circumstance we return below.

Before going further I wish to notice the following concerning other salts of organic acids as carbon food for *Azotobacter*.

Except with calciummalate there could be obtained an abundant or moderate growth with calciumlactate, calciumacetate and calciumpropionate, particularly when using canal water for the first infection. It was remarkable that the transport of a malate culture into lactate appeared to succeed nearly as well as of malate into malate, while even relatively rich crude cultures in propionate- or acetatesolutions, obtained directly from soil or water when inoculated into corresponding media, hardly grow on, if at all. This fact is the more remarkable

when we consider that by inoculation of a malate film into propionate or acetate as abundant cultures are obtained as in the said crude cultures in these media. But if it is tried to continue such cultures by re-inoculating anew into propionate or acetate they also soon lose their power of growth. From this we see that the preceding culture conditions to which the inoculation material has been subjected, are by no means indifferent to the vitality of the following generations, which are evidently very easily weakened and then nearly quite lose the faculty of fixing nitrogen. The importance of this fact cannot be denied and certainly deserves a nearer examination.

Calciumcitrate, calciumtartrate and calciumsuccinate, with either garden soil or canal water for infection, give but slowly a moderately developed bacteria film but it grows during a very long time. The film on the citrate is rich in spirilla and the *Azotobacter* form found in it differs in many respects from the ordinary varieties. In all these cases the quantity of bacteria grown during the first 2 or 3 weeks, is still too slight to necessitate a determination of the nitrogen, and could by a rough comparison with former computations be valued at some tenths of milligrams N_2 per gram of the dissolved lime salt. After a long time however, the fixation of nitrogen with these salts is also considerable.

With calciumglycolate in absence of nitrogen compounds no growth of microbes could be observed at all.

2. *Quantity of the fixed nitrogen.*

Neglecting for the moment the volatile acid, to which we shall return below, the analysis of the cultures is performed as follows.

The whole quantity of the liquid, in which are present the calciumcarbonate formed by oxidation from the malate or the other organic salt, besides the as yet not decomposed malate, the salt of the volatile acid, and the bacteria, is treated with a known quantity of normal hydrochloric acid by which the carbonic acid is expelled on heating; a then following titration with normal alkali and phenolphthaleine as indicator, shows how much calciumcarbonate is produced and consequently how much of the organic salt is oxidised.

After addition of a little sulphuric acid the liquid is evaporated to dryness and after KJELDAHL'S method examined on nitrogen, while in each of the materials used the rate of nitrogen is stated separately. The calciummalate of MERCK, Darmstadt, proved nearly free from nitrogen.

Now follows a table of some analyses¹⁾ which give an idea of the amount of nitrogen fixed through *Azotobacter*, when organic salts are used as carbon food. (See table).

These numbers show that the amount of nitrogen which can be fixed in the crude culture is at most 4.9 and 2.8 m.g. per gram of oxidised calciumsalt, obtained respectively with calciumpropionate and calciumacetate (experiment 10 and 11), while, per gram of calciummalate was fixed about 2.6 m.g. (experiment 2), and per gram of lactate 1.8 m.g. (experiment 9). It seems that the fixation goes on more rapidly at the beginning than later in the course of the experiment, whence it follows that when little of the organic salt is used proportionately more nitrogen is fixed than by larger amounts. This should be taken into consideration in judging the favourable results obtained with propionate and acetate, for then solutions were used with only 1% of the salt. As to these salts, they have proved to be in general an unfavourable source of carbon for *Azotobacter* if the *rapidity* of the growth is taken as indicator of the process, and only then to be able to give good results, when for the inoculation, cultures in malate solutions are used, in which a certain variety of our species is present. But also then, as observed above, already at the first passage from acetate into acetate the growth stops almost entirely. Pure cultures of *Azotobacter* develop hardly at all²⁾ in solutions of calciumacetate and natriumacetate, whatever may have been the conditions to which these cultures were previously subjected. Propionates and lactates still require a nearer investigation.

Of calciummalate, on the other hand, it has decidedly been proved that not only the crude cultures succeed very well and fix much nitrogen even at repeated passages in the same medium, but that this also holds good with regard to the pure cultures of *Azotobacter*. This is the first case in which I got the certainty that no other microbes are wanted, neither in the medium nor in the infection materials, but *Azotobacter* alone to cause the said phenomena. Various authors surely have repeatedly described the fixation of free nitrogen in pure cultures of *Azotobacter*, among others of late with respect to the acetates, but never had I been able to confirm the accuracy of these statements until I made a systematic investigation with calciummalate, a salt which had never before been used to this end, although I had

¹⁾ I owe to Mr. D. C. J. MINKMAN, assistant to my laboratory the determinations here referred to.

²⁾ The different varieties behave, however differently and some will begin to grow but the growth soon ceases.

already called attention to it as an excellent source of carbon for *Azotobacter* in my papers of 1902.

It must be allowed that the amount of fixed nitrogen in these pure cultures is not considerable, about 1.5 m.g. for each gram of oxidised malate, but perhaps here too, will be observed a greater production if only the very young cultures are examined; then, however, only little of the salt can be oxidised and the absolute quantities will of course be small.

It seems not superfluous here to call to mind that it is by no means the same whether a known amount of calciummalate be absorbed from a dilute solution or from a more concentrated one. In the latter case the malate will be more easily assimilable for the *Azotobacter* cells, which will induce a stronger oxidation and thus an increased oxygen assimilation in equal times, so that the tension of the oxygen in the liquid will be less than in the less concentrated solutions. As the growth of *Azotobacter* seems favoured by this lower tension, and in any case, a rather strong concentration of the carbon food proves favourable to the process of nitrogen fixation *in absolute quantity* this circumstance has been taken into consideration in all the experiments. Further, we did not always wait for the moment at which the malate had disappeared from the medium, but commonly it was much earlier subjected to the analysis for the reason mentioned above.

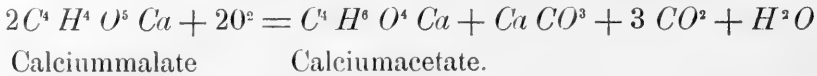
The observation that calciummalate can, glucose, cane-sugar and mannite on the other hand, cannot form the starting point for nitrogen fixation in liquid pure cultures, while yet the said carbon hydrates are in the crude cultures much more productive and may even give gains of nitrogen of 7 m.g. per gram of decomposed sugar, gives rise to the supposition that these carbon hydrates must previously be changed by other bacteria into organic acids and that these, at the moment of their production, serve as carbon food for *Azotobacter* and primarily cause the fixation of the nitrogen.

Of course it cannot be malic acid which hereby originates from the sugar; but the important growth of *Azotobacter* to which also the acetates, the propionates and lactates may give rise, suggest the question whether perhaps the acids of these salts may be first produced from the carbon hydrates and then govern the nitrogen fixation.

It is to be remarked that as well in the malate as in the lactate cultures slight amounts occur of a volatile acid, which will perhaps prove to be acetic acid, although it is has not been positively demonstrated by means of BEHRENS' uranylanatrium-acetate reaction. It is of importance to know that this volatile acid is not only found

in the crude, but also in the pure cultures of *Azotobacter*, so that it is certainly a product of this species itself.

In order to ascertain the amount of the volatile acid and the corresponding quantity of decomposed malate, it is supposed in the table to be acetic acid only and produced after the formula:



But it may also be formed without access of oxygen. The volatile acid is determined by distillation with sulphuric acid and silver sulphate and titration the distillate with normal alkali.

From the table we see that in the crude cultures nitrogen can without doubt be fixed with calcium acetate as carbon source. In truth we have not succeeded in effecting the same in pure cultures, but now that we have the certainty that *Azotobacter* alone, with malate as carbon food, is able to fix nitrogen, it must be admitted that this also holds good for the acetate cultures, although it is not clear of what nature is the assistance which other bacteria thereby must necessarily lend. Besides it should be noted that the fixation of nitrogen in the pure cultures, also when malate is used as carbon food, is less considerable than when other bacteria, too, can live on this substance at the same time.

3. *Distribution of Azotobacter in the soil.*

Earlier, already, I showed that it is possible to detect a few *Azotobacter* colonies among the thousands of those of the other species, when fertile garden soil is sown on mannite-kalium-phosphate plates. The use of calciummalate instead of sugar has proved to be of importance for the examination of the soil in this direction. First it should, however, be observed that no solid or liquid medium ¹⁾ could be found on which all the germs of *Azotobacter* sown out really develop into colonies. Thus, by sowing about 2400 germs (determined by microscopic counting), on various culture plates, 50, 12, 1, 30, 8, 20, 10, 20 and 75 colonies developed so that the growth in percents was only 2, 0.6, 0.5, 0.3, 0.3, 0.8, 0.4, 0.8 and 0.3. In another experiment were obtained of 10.000 germs sown on glucose-calcium-malate plates, 20, 25 and 48%, and on calcium-kaliummalate-plates 32.5, 36 and 65%. But in other cases, on agar plates with malate only the results were much better. The germs had

¹⁾ The use of thin layers of liquid media for colony-culture of microbes has been described in Centralblatt f. Bacteriologie, 2te Abt. Bd 20, 1908, p. 641.

been shaken up in sterile tap-water or in malate solutions, of which 1 cm³ was spread over the plate, care being taken that the water was quite taken up into the agar by its power of imbibition, which is easily effected by softly heating the plate so that the superfluous water evaporates.

We see from these data that *commonly* only a small part of the sown germs comes to growth. Whether perhaps the water itself has a deadly influence on some individuals, or that their death is caused by their passing on the solid medium, could not yet be made out by experiment. Thus, although there be ground to allow that more germs occur in the soil used than are found, the possibility exists that by continued investigation the experiment may be made so as to exclude that source of error.

But in spite of the uncertainty of the method the following result could be stated. By sowing a small quantity, for instance less than $\frac{1}{20}$ gram of garden soil on calciummalate-kaliumphosphate 1% agar, after 24 hours at 30° C. commonly no *Azotobacter* is observed, but a moderate number of moist colonies of about 1 mm. in diameter, first draw attention by their extension and prove to consist of different varieties of *Bacillus megatherium*, containing many spores. They don't cause any considerable oxidation of the malate and as the colonies no more grow after the second day, they evidently develop at the expense of the traces of nitrogen compounds which at first are present in the plates. After the second day a great number of *Streptothrix alba* appear. This microbe is so common in all the examined samples of soil that there can exist no doubt as to its either favourable or pernicious influence on the fertility; but the nature of this influence is as yet wholly unknown.

In a still later stadium the surface of the plate becomes covered with numerous relatively small colonies of bacteria, among which some species immediately draw attention by their extension and commonness.

The oxidation of the malate by all these microbes is slight, so that even after weeks the plates contain but little calcium carbonate, which seems almost entirely produced by the said larger colonies and by *Streptothrix*. All these species seem not to oxidise at all, or perhaps it is more accurate to say, not to oxidise any more after the last traces of fixed nitrogen have been assimilated. As to *Streptothrix*, from its relatively vigorous oxidising power it follows by no means that this should be associated with fixation of nitrogen; this species surely does not possess that faculty. If for the experiment soil is

used shaken from the roots of garden-plants, which are no Papilionaceae, the result is fairly the same; perhaps the number of the above mentioned oxidising forms is more numerous, but this is still doubtful.

Otherwise, however, is the result when the soil is examined which adheres to the roots of clover, pease, and beans when these plants are cautiously dug up. When the soil adhering to such roots is rubbed fine and after dilution in water sown on a malate plate we find, after a period of 2 days at 30° C., first that the said oxidising colonies have very abundantly developed. But, besides, among these colonies much larger ones are distributed, which oxidise much more vigorously and prove to belong to *Azotobacter*, which shows that a distinct relation exists between the distribution of this genus and the said Papilionaceae. Whether this relation will appear to be universal and what may be its signification, further experiments have to decide.

Chemistry. — “*Rapid change in composition of some tropical fruits during their ripening.*” By H. C. PRINSEN GEERLIGS.

(Communicated in the meeting of May 30, 1907).

Some tropical fruits which as a rule are gathered in a green and immature state and allowed to ripen afterwards, accomplish this ripening process so rapidly that within a few days they become tender, well-flavoured and palatable, thus offering a good opportunity for studying the still somewhat mysterious problem of the after-ripening of fruits.

I. *Phenomena during after-ripening.*

a. B a n a n a (M u s a).

As a rule the bunches of bananas, which contain fruits in various stages of maturity, are cut from the plant as a whole when all the fruits are still green and are hung up to ripen. At the moment when the bunch is cut none of the bananas are fit for food; they are hard, tasteless and flavourless, the skin is thick, contains much latex and tannin and adheres to the fleshy part. After a few days the skin becomes thin and yellow and can easily be detached, whilst the edible matter is now tender, sweet and well-flavoured. A couple of days afterwards the fruit is unpalatable again owing to overripeness and decay which change it into a soft mass.

This after-ripening is accompanied by a considerable loss of weight as is shown by the following figures.

20 bananas broken from the bunch in a green state were placed in a relatively cool spot (28° C.) and weighed daily.

The average weight per fruit was :

after 0	1	2	3	4	5	6	7	days
145	143	142.5	142	141	139	138	137	grammes.

Further, 10 green bananas of another variety were placed under a glass bell jar into which a current of air free from carbonic acid was introduced. The air leaving the bell jar was made to pass through a drying apparatus and a Liebig potash bulb, which latter was daily weighed.

The fruits weighed originally	502.5	grammes
and after 4 days only . .	487.0	„
therefore lost in weight . .	<u>15.5</u>	grammes

The weight of the potash bulb increased

the first day by	0.065	grammes
the second day by	1.455	„
the third day by	0.540	„
the fourth day by	<u>0.240</u>	„

Total increase 2.300 grammes

So that the fruits gave off 2.3 grammes or 0.44 % of carbonic acid in four days.

The chemical changes taking place during the after-ripening process were now studied. Each day a banana was broken off from a green unripe bunch of the fruit and when doing this care was taken to select the specimen from the same row of the bunch from which the previous one had been taken and thus to obtain samples of the same initial ripeness. The fruit was first peeled and rubbed to pulp in a mortar. I determined the amount of moisture by drying 10 grammes to a constant weight. Next 100 grammes of the pulp were extracted with alcohol and the residue dried and weighed. I evaporated the alcoholic solution after addition of a little calcium carbonate with the object of neutralising the acids. The residue was dissolved in water, additioned with a little solution of neutral lead acetate and made up with water to 100 cM³ in order to get the sugars in the solution in the same concentration as that in which they originally were present in the pulp. I determined polarisation and reducing sugar in this solution both before and after inversion and calculated from the figures obtained the amount of sucrose, glucose and fructose

after having stated that no other sugars were present in the liquid.

I pulverised the dried residue left behind after the alcoholic extraction of the pulp and extracted part of it with cold water. This extract was evaporated to a small volume and precipitated with alcohol. The precipitate was collected on a weighed, ashless filter washed with alcohol, dried, weighed, incinerated and the loss of weight occasioned by the combustion of organic matter was recorded as dextrin after I had convinced myself by the red coloration which iodine solution produced in the solution of such a precipitate that it really was dextrin.

A second portion of the residue was hydrolysed with hydrochloric acid under pressure and the amount of glucose thus obtained calculated as starch. Finally, I determined the percentage of nitrogen and calculated from this figure the amount of albuminoids by multiplication with the factor 6,25. The figures for the different analyses follow here:

Date of the analysis	17th April	19th April	20th April	22d April	23d April	24th April
Degree of maturity	Unripe the skin adheres to the fruit	Unripe the skin loosens	Begins to ripen	Alm. ripe	Ripe	Over- ripe
% Skin	45	44	43	39	37.8	36.2
% Fleshy matter	55	56	57	61	62.2	63.8
<i>Composition of the pulp</i>						
Moisture	58.24	59.21	59.48	59.86	60.88	61.12
Dry substance	41.76	40.79	40.52	40.14	39.02	38.88
Insoluble in alcohol	39.41	34.06	29.58	20.98	15.30	13.00
Soluble in alcohol	2.35	6.73	10.94	19.16	23.72	25.88
Sucrose	0.86	4.43	6.52	10.50	13.68	10.36
Glucose	} 0.25	0.96	1.80	3.18	4.72	6.1
Fructose		0.90	1.53	2.70	3.61	4.8
Dextrin	trace	0.52	0.59	0.69	0.65	0.65
Starch	30.98	24.98	20.52	13.81	9.59	7.68
Albuminoids	2.65	2.60	2.60	2.58	2.58	2.55
Ash	0.94	0.96	0.97	0.95	1.00	1.01

The skin contains much rubber, fibre and also a small amount of

soluble carbohydrate and its composition calculated in 100 parts of dry substance does not vary considerably in the green and in the ripe state. The water content, however, diminished greatly during ripening so that the shrinkage of the skin is chiefly due to loss of water.

The analysis of the pulp shows large differences during the after-ripening because of the starch being rather suddenly transformed on a large scale into sucrose.

That the sugar present in the ripe fruit was really sucrose was proved by evaporating to a small volume the clarified alcoholic extract from fully ripe bananas and allowing it to crystallise. After some time it deposited crystals which were recognised to be sucrose by numerous chemical and physical tests. In the ripe fruits this sucrose becomes partly inverted or consumed by the aspiration either as such or as products of its inversion. The latter possibility is the more probable one, as, first of all, much carbonic acid is formed during the after-ripening and secondly because the fructose is in every case present in a smaller proportion than the glucose. It is evident, therefore that these two constituents are not consumed together as sucrose, but separately after the splitting up of that body and then the fructose more readily so than the glucose.

During the saccharification process a little dextrin is formed too.

b. Mango (Mangifera).

The mango fruit, as a rule, is picked when still unripe; in this state the fruits are internally white, hard, acid and flavourless, but within a few days they undergo an after-ripening process which renders them tender, full-flavoured, and yellow or orange-coloured.

This period is, as in the former case, soon followed by over-ripeness and decay.

A few mango fruits, of a variety which bears very sweet and well-flavoured fruits when ripe, were picked green, placed on a cool spot at a temperature of 28° C. and weighed every day with this result

Nº.	29th Sept.	1st October	2d October	4th October
I	247 Gr.	243 Gr.	241 Gr.	240 Gr.
II	229	226	224	223
III	227	223	222	219.5
IV	249	247	246	244

Five green mangos were weighed and placed under a glass bell jar, through which a current of air free from carbonic acid was conducted which afterwards was made to pass through a Liebig potash bulb.

This latter was weighed daily and the 5 fruits only after the end of the experiment.

The 5 fruits weighed originally	1139.3 grammes
After 3 days	1121.3 „

and therefore lost in 3 days	18.0 grammes
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The potash bulb increased during	
the first day by	1.712 grammes
the second day by	1.276 „
the third day by	1.570 „

Or in three days	4.558 grammes
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The fruits gave off 4.558 grammes or 0.40% of carbonic acid in three days.

Just as in the case of bananas a mango fruit from a parcel having practically the same initial maturity was daily analysed; and this time the analysis extended with a determination of free and total citric acid. I had previously stated that the acid in the mango really was citric acid and that no other organic acid could be found in it.

I determined the free citric acid by titration with 1/10 normal potash in the boiled fruit whilst the amount of total citric acid was determined by extracting the boiled fruit with alcohol and precipitating the citric acid in the alcoholic liquid by means of barium acetate. The precipitate was filtered off, washed, incinerated and finally, I determined the carbonic acid in the ash which was of course equivalent to the total citrate in the precipitate. The figures obtained follow here.

The yellow colouring matter, which is produced during the ripening process, shows the same reactions as the carotene from carrots, the same spectroscopic appearance and in fact resembles it in every respect.

During the after-ripening the starch is transformed into sucrose, which later on becomes hydrolysed and splits up into glucose and fructose. In the beginning of the process the fruit liberates water but this constituent increases afterwards owing to the combustion of the carbohydrates. The citric acid is vigorously attacked and the decrease in the acid taste during the after-ripening is not due to an increase

Date of the analysis	29th Sept.	1st October	2d October	4th October
Degree of maturity	Unripe	Almost ripe	Ripe	Over ripe
Moisture	83.34	82.95	81.95	83.20
Dry substance	16.66	17.05	18.05	16.80
Soluble in alcohol	6.36	15.18	15.54	14.70
Insoluble in alcohol	10.30	1.87	2.51	2.10
Sucrose	2.57	10.50	12.27	9.31
Glucose	0.60	1.53	1.30	2.10
Fructose	1.90	2.10	2.01	2.60
Starch	8.53	0.55	0	0
Free citric acid	1.36	0.34	0.25	0.10
Total citric acid	1.31	0.37	0.21	0.10
Ash	0.42	0.44	0.41	0.43
Albuminoids	0.80	0.80	0.75	0.73

in the sugar content, nor to a neutralisation of the acid but solely to combustion and thus destruction of the organic acid itself.

C. *Tamarind* (*Tamarindus*).

The tamarind fruits remain on the tree until they are fully ripe and thus do not undergo any after-ripening process after being plucked or shaken off. In the unripe state the flesh is white and hard and fills the whole pod so that the woody skin is firmly attached to it. Later on, when the fruit ripens, the flesh becomes tender and brown and owing to evaporation, shrinks in such a way that a large empty space exists between the dry pulp and the hard skin. The composition of the pulp of tamarind fruits in several stages of ripeness is given here. (see p. 80).

In this case too the starch has become transformed into sugar, during the ripening but this time not into sucrose, but into a mixture of glucose and fructose. At the same time a great deal of water was evaporated, causing the fruit to shrink in its envelope and finally much acid was consumed by respiration, since the amount of total tartaric acid in the desiccated fruit was smaller than that in the so much more juicy one of a month before. The increase of the percentage sugar after the period of maturity is due to the

Date of the analysis	11th May	27th May	20th June	15th July
Degree of maturity	Green	Almost ripe	Ripe	Dessicated
Dry substance	15.86	38.46	40.92	76.20
Moisture	84.14	61.54	59.08	33.80
Glucose	0.40	10.10	20.4	25.10
Fructose	0.33	5.10	11.6	10.6
Fibre and pectin	3.27	8.10	7.90	14.57
Starch	3.33	1.25	0	0
Free tartaric acid	3.25	15.8	14.6	—
Total tartaric acid	4.85	18.1	16.4	14.4
Potassium bitartrate.	4.00	5.76	4.50	—

strong concentration by evaporation, because no fresh formation of sugar can possibly have taken place in so dry a fruit.

d. Sapodilla (Achras sapota)

The fruits are plucked tree-ripe; in which state they are green and hard, and contain tannin and gutta-percha dissolved in the sap, which render the fruit unfit for eating. After they have been preserved in bran, the gutta-percha as well as the tannin, become insoluble and the fruit itself gets tender, full-flavoured and palatable. On examining sections of the fruit one sees the coagulated gutta-percha as a series of white strings, while the tannin is deposited as insoluble matter in some cells.

The analyses of such fruit in a tree-ripe and full-ripe condition are given here.

	Tree-ripe	Full ripe
Moisture	74.76	75.20
Dry substance	25.24	24.80
Sucrose	7.80	7.02
Glucose	2.85	3.7
Fructose	2.70	3.4
Starch	Absent	Absent
Pectine	3.34	4.00
Albuminoids	0.45	0.40
Ash	1.50	1.50

Unlike the after-ripening of the former three fruits, this one is not due to saccharification of starch. The amount of sugar before and after the full ripening is the same, but in this case the fruit has become palatable by the softening of the hard pectin and by the deposit of tannin and gutta-percha from the juice as insoluble bodies.

I have to mention here that I did not find lactose in this fruit which has been stated by BOUCHARDAT as being one of its constituents. They, however, contain much pectin and owing to the presence of this body the juice yielded a fair amount of mucic acid on oxidation with nitric acid; this renders the supposition probable that this acid, considered by BOUCHARDAT as an evidence of the presence of lactose, has simply come from the pectin.

II. Agents of the saccharification during after-ripening.

When studying the fruits which come first into account in the research under consideration, viz. the banana and the mango fruit, we found in a certain stage of the development a rather sudden transformation of starch into sucrose, followed in a later stage by inversion and partial transpiration of the products of inversion. From experiments on the determination of the carbonic acid in the atmosphere in which this sudden transformation took place, I came to the conclusion that just the period of the rapid saccharification coincided with a strong development of carbonic acid, or with a powerful oxidation and degradation. At the same time the moisture on the inside of the glass bell jar in which the fruits ripened showed that a copious evaporation had accompanied the oxidation.

The figures for the carbonic acid from the bananas showed on the second day a strong development which decreased very soon, whilst those for the mangos remained somewhat stationary for the three days under observation. These data correspond very well with the more rapid after-ripening of the former fruits during this experiment in which they turned from green into yellow even on the second day.

The transformation is therefore accompanied by oxidation and I tried to check it by excluding the fruits from the free access of oxygen. To this end I covered a few green mango and banana fruits with collodion and kept them together with a few similar fruits not covered with an impermeable layer. The fruits covered with collodion did not ripen well, and were converted into decayed masses, while locally the wrinkles occasioned by the dying off of the fruit caused the collodion layer to burst and thus made the experi-

ment unreliable. Moreover it might well be that the decay was not only to be ascribed to the exclusion of oxygen but to the hindered evaporation which would be injurious to the fruit.

In order to elucidate this point, a few bananas were placed in a tube, through which a current of nitrogen passed, while at the same time some other bananas from the same part of the bunch were kept in the ordinary atmosphere. When the latter had become yellow, tender and ripe, those in the nitrogen tube had still retained their green appearance. The analyses of the peeled fruits of the two parcels yielded these figures.

	In nitrogen	In air.
Moisture	70.54	68.36
Insoluble in alcohol.	25.90	11.06
Soluble in alcohol.	3.57	20.58
Sucrose	0.31	13.66
Reducing sugars	0.94	4.80

It followed then, that the after-ripening in the air had gone on uninterruptedly whilst the fruits kept in the nitrogen atmosphere had remained unchanged and had preserved their starch content; so that free access of oxygen is an indispensable condition for the saccharification of starch in the fruit.

The following experiments were undertaken with a view to ascertaining whether this saccharification was brought about by a vital process or by the action of some diastatic ferment present in the fruit.

A jelly consisting of isinglas and agar agar of such a composition that it was solid at the ordinary temperature was mixed with 1% of starch, poured into a series of Petri dishes and sterilised. Slices of green mango and banana fruit or pieces of half ripe tamarind fruit were placed on the stiff jelly in some dishes and on that of others figures and letters were traced with a pencil dipped in mango-juice. After two, or sometimes more, days the particles of fruit were removed and the jelly covered with a very dilute solution of iodine in potassium iodide which after having remained there for a minute was washed off. In every case not only the spot where the fruit had been placed or where the pencil strokes had been applied, remained white, but all round a white stain spread out, lined with a red border which gradually faded into the surrounding blue coloration of the still unattacked starch. The longer the dishes had been allowed to stand, the larger was the white stain. In every one of these cases,

therefore, a diastatic ferment had diffused from the fruits and from the juice, which had transformed all the starch, it could get hold of through the state of dextrin into sugar.

When the iodine solution was allowed to act too long on the jelly, the iodine penetrated through the surface layer and reached the lower one, where the starch was still unattacked, thus colouring the whole dish blue. Finally pieces of banana and tamarind fruit were placed on slices of sterilised potato; the result was that the saccharification of the starch caused more or less deep cavities to appear in the places where the fruits had been applied.

All this however is not yet a direct proof that the saccharification has been occasioned by a ferment; and in order to make this clear I immersed slices of banana into alcohol, left them there during a couple of days, then took them out, expelled the alcohol by means of a current of sterilised air and placed them again in Petri dishes on a layer of starch emulsion stiffened with isinglass and agar agar. Though not so rapid as in the case of the much more juicy fresh fruit, yet also here the ferment diffused through and after the application of the iodine solution the white stains with the red borders became visible.

A quantity of mango juice was added to a boiled and re-cooled solution of 3% starch at 50° C. and kept at that temperature for some time. The liquid, which, at the outset, had given a deep blue reaction with iodine solution only became red when at the end of the experiment this test was repeated; this coloration did not undergo any change even if the mixture was kept for some time longer or if a fresh quantity of mango juice was added. The total amount of sugar, contained in the liquid (for the mango juice itself had also contained sugar) was higher after the reaction than before, which showed that the mango juice had contained a diastatic body with power to transform starch into dextrin and into sugar.

Now the question still remained which sugar is formed in the laboratory outside of the living organism.

The ripening fruits and their juices already contain so much sugar, which mixes with the small amount of sugar formed by the saccharification of the starch that the proper identification of that latter portion is extremely difficult if not impossible.

In order to eliminate the influence of the already existing sugar, ripening banana fruits were peeled and repeatedly triturated with alcohol and the extracted pulp, which contained as little sugar as possible was pressed and brought into glycerin. After a few days the amount of sugar and its nature was ascertained in the glycerin by

polarimetric and copper tests both before and after inversion. Next 100 grammes of this glycerin were mixed with a 3% starch solution, warmed to 40° C. and kept at that temperature for a couple of hours. After that the dissolved starch and dextrin was precipitated with alcohol, filtered, a pinch of calcium carbonate was added to the filtrate to prevent inversion by the slightly acid reaction of the filtrate, and the alcohol was evaporated off. The syrupy residue was dissolved in water, diluted to the volume of 100 cM.³ and used for the determination of the sugars by the polarimeter and Fehlings solution before and after inversion.

The original glycerin solution had contained 0.17% of glucose both before and after inversion, while after the treatment with starch 100 grammes of the solution contained 0.60 grammes of reducing sugars before inversion and 0.67 after that operation, which shows that 0.43 grammes of glucose and 0.07 grammes of sucrose (?) have been formed from the starch by the ferment. The polarisation of the solution was +0.9 before and +0.4 after inversion, giving evidence, that notwithstanding the precipitation with alcohol, a small amount of starch or dextrin has still remained dissolved.

At any rate from the fact that the exclusion of oxygen prevents the saccharification of the starch in the fruit and from the negative results of the experiments on formation of sucrose by means of fresh juice and of the precipitated and re-dissolved ferments, it follows that the rapid transformation of starch into sucrose during the after-ripening of some fruits is a vital process and not a consequence of the action of some ferment contained in the fruit which, just as diastase forms maltose from starch, could be isolated to form large quantities of sucrose from any kind of starch in the laboratory.

Mathematics. — “*Congruences of twisted curves in connection with a cubic transformation.*” By Prof. JAN DE VRIES.

(Communicated in the meeting of May 30, 1908).

§ 1. If x_1, x_2, x_3, x_4 are the coordinates of a point X with respect to a tetrahedron having O_1, O_2, O_3, O_4 as vertices, then

$$x_1 x'_1 = x_2 x'_2 = x_3 x'_3 = x_4 x'_4$$

determines a cubic transformation which transforms the right line

$$x_k = \lambda a_k + \mu b_k$$

into a twisted curve ω^3 , represented by

$$x'_k = \frac{1}{\lambda a_k + \mu b_k}.$$

The congruence Γ of the curves ω^3 through the five points

O_k ($k=1, 2, 3, 4, 5$) is now transformed into a sheaf of rays having as vertex the point O'_5 conjugate to O_5 .

To the bisecant b' through O'_5 of the curve σ'^5 brought arbitrarily through O_1, O_2, O_3, O_4 , corresponds a β^3 through O_1, O_2, O_3, O_4, O_5 , having the right line s as chord.

The following will show that the indicated transformation enables us to deduce by a simple method a number of well-known properties of systems of curves ω^3 .

§ 2. Let us consider the curves ω^3 of the congruence Γ cutting the right lines l and m . They are transformed into the right lines through O'_5 , resting on two curves λ'^3 and μ'^3 . Now the cubic cones, projecting these curves out of O'_5 have besides the right lines $O'_5 O_k$ ($k=1, 2, 3, 4$) five edges more in common, which are the images of as many twisted curves belonging to Γ .

From this is evident that the curves of Γ cutting a given right line l form a *surface A^5 of order five*.

The image of A^5 is a cubic cone, projecting λ'^3 out of O'_5 and having the bisecant b' out of O'_5 as nodal edge. Therefore the curve β^3 of Γ having l as bisecant is a *nodal curve* of A^5 .

If we bring the right line m through O_1 its image is a right line m' passing likewise through O_1 and having therefore with the above mentioned projecting cone of λ'^3 besides O_1 two points in common. From this we conclude that A^5 has *five threefold points* O_k .

So the section of A^5 with $O_k O_l O_m$ consists of the right lines $O_k O_l, O_l O_m, O_m O_k$ and a conic through O_k, O_l, O_m cutting $O_p O_q$ and forming with this right line a cubic curve of Γ . Consequently *eleven right lines and ten conics* lie on A^5 .

§ 3. The curves ϱ^3 of Γ touching a given plane φ , are transformed by the correspondence into tangents t' through O'_5 of a cubic surface Φ'^3 having conic points in O_k ($k=1, 2, 3, 4$). The polar surface of O'^5 passes through the four double points O , so it has as image a quadratic surface through those points. The section of the latter with φ is the image of the locus of the points, in which Φ'^3 is touched by the right lines t' . *This conic* contains therefore the points in which φ is *touched* by the curves ϱ^3 .

Through O'_5 pass six principal tangents of Φ'^3 , the congruence Γ contains therefore *six curves, osculating φ* .

The enveloping cone φ'^6 out of O'_5 to Φ'^3 has four nodal edges $O'_5 O_k$; for a plane through $O'_5 O_k$ cuts Φ'^3 according to a cubic curve

with node O_k , sending but four tangents through O'_5 , so that in that plane $O'_5 O_k$ replaces two edges of the cone.

So φ'^6 has with an arbitrary cubic curve through the four points O_k ten points in common lying outside O_k . By applying our transformation we find from this that the curves of Γ touching φ form a surface Φ^{10} of order ten.

A right line through O_1 cuts φ'^6 in four more points; on its image therefore rest four curves ϱ^3 touching φ . From this ensues that Φ^{10} has five sixfold points O_k .

The right lines $O_k O_l$ lie therefore on Φ^{10} ; it can as follows become evident that they are *nodal rightlines*. A right line resting on $O_1 O_2$ and $O_3 O_4$ has six points in common with φ'^6 . So its image must have on $O_1 O_2$ and $O_3 O_4$ four points in common with Φ^{10} .

The section of Φ with $O_1 O_2 O_3$ consists of the right lines $O_1 O_2$, $O_2 O_3$, $O_3 O_1$ to be counted double and a curve of order four, having nodes in O_1 , O_2 , O_3 and in the point of intersection of the nodal line $O_4 O_5$; thus it consists of two conics. These conics form evidently with $O_4 O_5$ two cubic curves of Γ , touching φ .

Consequently there lie on Φ^{10} ten *nodal lines and twenty conics*.

When we regard the tangential cones out of O'_5 to two quadri-nodal cubic surfaces Φ'^3 it follows readily that Γ contains *twenty* curves touching two given planes.

§ 4. To determine how many curves ϱ^3 can be brought through four points O_k having the right line b as bisecant and resting on the right lines c and d , we have but to find the number of right lines r' which cut β'^3 two times and γ'^3 and σ'^3 one time, when these three curves have four points O_k in common.

Now the chords of β'^3 resting on a right line l form a biquadratic scroll on which β'^3 is nodal curve, having thus with γ'^3 besides the four points O four more points in common. From this follows immediately that the right lines cutting β'^3 twice and γ'^3 once also form a biquadratic scroll Σ'^4 . The cones which project these curves out of a point of β'^3 having two edges in common, not containing one of the points O , the curve β'^3 is also nodal curve on Σ'^4 . With σ'^3 this scroll has besides O_k four points in common; so on γ'^3 and σ'^3 rest four chords of β'^3 , and by applying the transformation we find that the curves ϱ^3 which cut b twice and c once form a surface Σ^4 of order four.

If we bring d through O_1 , then its image d' has with Σ^4 two more points in common; consequently d cuts the surface Σ^4 in two points lying outside O_1 , so that O_1 is a node. Therefore the surface Σ^4 has *four double points* O_k .

Evidently b is nodal right line of Σ^4 ; for, b is the image of the nodal curve β^3 lying on Σ^4 .

Through a point S of b pass two curves ϱ^3 ; their two points of intersection S' and S'' with b are the points which b has still in common with the surface \mathcal{A}^5 determined by c , S and the points O .

As the pairs of points S and S' form a (2,2) correspondence, *four* curves ϱ^3 can be brought through four points, which *touch* a right line and *intersect* another right line.

The section of Σ^4 with the plane $O_1O_2O_3$ has nodes in O_1, O_2, O_3 and in the intersection with b ; so it consists of two conics. One of these conics contains also the intersection of c ; it is completed to a degenerated ϱ^3 by the right line out of O_4 resting upon it and upon b . The second conic contains the intersection of the transversal drawn out of O_4 to b and c and forms with this right line a ϱ^3 .

On the surface Σ^4 lie therefore *eight conics, nine simple right lines and a nodal line.*

§ 5. The number of curves ϱ^3 through O_k ($k = 1, 2, 3, 4$) resting on the right lines a, b, c, d is evidently as large as the number of transversals of four cubic curves $\alpha^3, \beta^3, \gamma^3, \delta^3$ brought through O_k . The scroll (α, β, l) , having α^3, β^3 and a right line l as directrices, is of order 14, l being fivefold and each plane through l containing nine right lines. If l_0 passes through O_1 a plane through l_0 contains but four right lines, so that the order of the scroll (α, β, l_0) amounts but to 9. From this ensues that (α, β, l) possesses four twofold points O_k .

With γ^3 the scroll (α, β, l) has 22 points in common outside O_k ; so (α, β, γ) is of order 22.

On the scroll (α, β, l_0) we find that O_1 is fivefold, because a right line through O_1 cuts four generatrices; on the other hand O_2, O_3 and O_4 are threefold points, for a right line through O_2 cutting the fivefold right line l_0 , meets but *one* generatrix more. With γ^3 the scroll (α, β, l_0) has still $9 \times 3 - 5 - 3 \times 3 = 13$ points in common besides the multiple points. In connection with the above follows from this that O_1 is a ninefold point on (α, β, γ) .

Of the points of intersection of (α, β, γ) with δ^3 36 lie in O_k ; consequently $\alpha^3, \beta^3, \gamma^3, \delta^3$ have thirty common transversals.

Therefore we can bring through *four* points *thirty* cubic curves resting on *four* given right lines.

§ 6. Let us now consider the surface Ψ^{30} formed by the curves ϱ^3 resting on a, b and c . Through a point A of a and the points O

pass five ϱ^3 cutting b and c . From this is evident that a , b and c are *fivefold right lines*.

With a right line m through O_k the scroll (α, β, γ) has thirteen points lying in O_k in common, so its image m' (right line through O_k) cuts ψ^{30} likewise in 13 points lying outside O_k . We conclude from this that the four points O are *seventeenfold* on ψ^{30} .

So the right lines $O_k O_l$ lie on this surface; that they are *fourfold right lines* can be shown in this manner.

As O_k and O_l are *ninefold* on (α, β, γ) the right line $O_k O_l$ is cut outside those points by $22 - 18 = 4$ transversals of the curves α, β, γ ; the images of these right lines are conics through O_k and O_l resting on $O_m O_n, b, c$ and d and forming with $O_m O_n$ a ϱ^3 of the system.

The section of ψ^{30} with $O_1 O_2 O_3$ can consist outside the three *fourfold right lines* only of *conics*; these are easy to indicate. In the first place we can bring through O_1, O_2, O_3 a conic cutting b and c ; it is completed to a ϱ^3 by each of the two right lines out of O_4 resting on the conic and on d . Then the sections of d and of the transversal with O_4 to b and c with O_1, O_2, O_3 determine a conic forming with the indicated transversal a ϱ^3 . So we have in O_1, O_2, O_3 three *double* and three *simple conics*; with the three *fourfold right lines* they form a section of order 30.

On ψ^{30} lie therefore 4 *seventeenfold points*, 3 *fivefold*, 6 *fourfold* and 36 *simple right lines*, 12 *double conics* and 36 *simple conics*.

Astronomy. — “*Contributions to the determination of geographical positions on the West coast of Africa. III.*” By C. SANDERS.
(Communicated by E. F. VAN DE SANDE BAKHUYZEN).

(Communicated in the meeting of May 30, 1908).

I. Introduction.

After a stay in Europe during the winter 1902—1903 I returned to Portuguese West Africa and remained there until the autumn 1906 when I again went to Europe for some time.

During this period 1903—1906 I have once more tried to contribute to the determination of geographical positions in these parts as much as time and circumstances allowed. Circumstances, however, were often unfavourable to my observations, and hence the results obtained are less than I had desired and expected at first.

The results obtained may be ranged under three heads.

1. *New determinations at Chiloango.* In November and December

1903 I made here a new series of determinations of latitude by means of zenith distances in the meridian. But I did not succeed in securing new data with which to correct the determination of the longitude, and at last I have entirely given up this plan, until I should possess a telescope of the required dimensions for the observation of occultations of stars¹⁾, because the observations of the latter will certainly lead to a greater accuracy in the determination of the longitude than can be attained by means of lunar altitudes with my relatively small instrument.

2. *Determinations of astronomical coordinates at different stations in the Chiloango district.* On two journeys, one to N'Kutu on the upper course of the Chiloango river from 22 to 31 December 1903 and a longer journey through Mayombe²⁾ in June 1904, I was able to make determinations of latitude and longitude. The reason why these could not be made oftener lies chiefly in the peculiar difficulties attached to the transportation of the instruments especially of the chronometers. The best way of transporting them is by water by means of a canoe, and even then one must constantly pay attention to avoid shocks caused by trees floating down the river. When the chronometers had to be transported by land, I used a hammock suspended from a long stick carried by two negroes; while mounting hills they tried to keep the stick as much horizontal as possible.

Another circumstance which makes it difficult to obtain accurate results is that these excursions can be undertaken only during the dry season, when the nightly sky is as a rule overcast, so that one must take recourse to observations of the sun, and lastly in many parts one meets with great difficulties in finding a proper dwelling place, because prosperous negro villages, which formerly existed, are almost entirely depopulated and turned into desert in consequence of the trypanosomosis, which has raged there.

On my journey in December 1903 the instruments were entirely transported by water, first by steamer to Mayili then by canoe to N'Kutu. At this latter station I secured determinations of latitude and longitude.

The journey through Mayombe in June 1904 also began by steaming up the Chiloango- (or Loango-) river to Mayili. We there arrived on June 2 and I made a time determination in order to control the longitude determined previously. We then travelled by land to

¹⁾ I received for some time past (1907) a telescope of ZEISS of 80 mm. aperture and 120 cm. focal length, with which I have already made some experiments.

²⁾ The name of a part of the Chiloango district.

Chimbete (June 3) and then per canoe up the river to N'Kutu. The first transport by land, when the carriers were not yet accustomed to their uncommon task, unfortunately caused a perturbation in at least one of the two chronometers, which appeared from the comparisons between them.

Also at N'Kutu I made a time determination on June 5, in order to obtain another result for the longitude of that place. On June 6 we continued our journey by land often along very difficult roads through woods and over hills and some times across small streams. We first went to the north east as far as N'Vyellele, a village 28,5 kilometers north east of N'Kutu (June 7), and then we travelled to the west during three days until June 10, when we reached Buku-Zan, a village on the Luali, a tributary river of the Loango.

On June 13 and 14 we made an excursion from Buku-Zan to the north to M'Pene Kakata, but the rest of the time until June 16 I stayed in the former place and availed myself of this opportunity to determine its longitude and latitude.

On June 16 we returned from Buku-Zan to N'Kutu. This time we went directly to the south east, and after we had covered a distance of 38 kilometers we arrived at N'Kutu on June 17. Thence we returned by the way we had come via Chimbete and Mayili to Chiloango (18—23 June). In the mean time I secured determinations of latitude and longitude at Chimbete.

3. *Connection of a great number of secondary points with the astronomically determined stations, by means of compass directions and distances.* It was my intention to form by means of my astronomical determinations a net of primary points with which I might connect a great number of intermediate points whose relative positions I had determined on many journeys by means of compass directions and distances, in order thus to reach also for the latter a satisfactory accuracy. In this I have partly succeeded, but for the southern part of the district it is still necessary to make the astronomical determination of one and if possible 2 stations on the Lukula river, Chipondi and perhaps Pouro, the more so as the preliminary result of my secondary determination of the station Lemba on this river differs much from that which Mr. CABRA had obtained some years ago, when he determined the demarcation between the Freestate and Portuguese Congo.

I shall try to fill up this gap. But the difficulties are especially great in these parts, as the trypanosomosis has badly raged here of late. At any rate it will be desirable to put off till later the communication of my secondary determinations.

CORRECTIONS AND RATES OF THE CHRONOMETERS.

Date	M. T.	Temp. C.	Chron. Hewitt			Chron. Hohwū	
			Corr.	D. Rate	D. Rate 20' C.	Corr.	D. Rate
1903 May 15	h 8 12		m s +47 59 03			m s +46 55 03	
" 20	8.15	24.5	58.38	s -0 13	s -1 25	56.38	s +0 27
" 25	8.46	24 0	57.24	-0.23	-1.23	57.24	+0.17
June 20	8.18	22.0	58.13	-0.74	-1 24	48.13	-0.35
" 27	8.10	19.6	31.41	-0.96	-0.86	45.41	-0.39
July 3	8.32	19.6	26 06	-0.89	-0.79	40.06	-0.89
" 10	8.25	19.7	18 71	-1.05	-0.97	32.71	-1.05
" 17	8.10	20.1	11.17	-1 08	-1 10	27.57	-0.73
" 25	8.50	19.1	1 98	-1.15	-0.93	20.48	-0.89
Aug. 4	8.15	9.7	+46 51.06	-1.09	-1.01	15.06	-0.54
" 24	8.22	21.0	41.03	-0.50	-0.52	8.53	-0.33
Oct. 12	8.45	24.4	41.88	+0.02	-1.08	13.38	+0.10
" 19	8.10	25.6	44 45	+0.37	-1.03	17.95	+0.65
Nov. 5	7.93	25.5	54.35	+0.58	-0.80	21 85	+0.23
" 16	8.53	26.0	+47 2.31	+0.72	-0.78	22.81	+0.09
" 20	7.98	25.6	4 32	+0.50	-0.90	23.92	+0.28
Dec. 20	8.05	25.3	17.97	+0.46	-0.86	48.97	+0.83
1904 Jan. 3	8.04		28.08	+0.72		52.08	+0.22
" 6	8.43	25.3	28.70	+0.21	-1.11	53.20	+0.37
" 17	7.97	25.7	35.56	+0.62	-0.80	+47 0.56	+0.67
" 22	8.20	25.4	37.35	+0.36	-0.99	5.35	+0.96
" 29	8 44	25 2	40.79	+0.49	-0.81	10 79	+0.78
Febr. 9	8.40	25.3	45.93	+0.47	-0.85	19.43	+0.78
" 20	8.05	25.8	55.41	+0.86	-0.59	21.41	+0.18
March 4	8 23	25.8	+48 8.69	+1.02	-0.43	30.69	+0.71
" 31	8.08	25.7	38.47	+1.10	-0.32	43.47	+0.47
May 12	8.08	25.5	+49 13.51	+0.83	-0.55	+48 8.01	+0.58
" 23	7.80	24 5	14.83	+0.12	-1.00	18.33	+0.94
" 30	8.37	24.4	15.66	+0.11	-0.99	26.66	+1.18
June 24	7.70		22.83	+0.29		47.33	+0.83
Aug. 1	8.30	20.9	17.42	-0.14	-0.36	+49 8.92	+0.57
Sept. 30	7.90	21.2	+48 58.86	-0.31	-0.61	20.86	+0.20
Oct. 14	8 24	23.8	+49 1.48	+0.19	-0.79	25.98	+0.37

Date	M. T.	Temp. C.	Chron. Hewitt			Chron. Hohwü		
			Corr.	D. Rate	D. Rate 20° C.	Corr.	D. Rate	
		h	m s	s	s	m s	s	
1904 Oct.	24	8 30	24.3	+49 5 35	+0 39	-0 69	+49 33 85	+0 79
Nov.	5	8.25	24.6	10.03	+0.39	-0.76	42.03	+0.68
"	10	8.25	25.1	11.93	+0.38	-0.90	44.93	+0.58
"	18	8.07	25.1	15.25	+0.42	-0.86	51.75	+0.85
"	29	7.99	25.5	19.97	+0.43	-0.95	+50 3.97	+1.11
Dec.	9	8.10	25.1	26.46	+0.65	-0.63	11.96	+0.80
"	19	8.32	25.0	28.54	+0.21	-1 03	22.04	+1.11
1905 Jan.	2	8.12	24.6	31.26	+0.19	-0.96	24.26	+0.87
"	14	8.10	25.7	36.40	+0.43	-1.01	46.40	+1.01
"	21	9.24	25.6	38.64	+0.32	-1.08	52.14	+0.82
Febr.	12	8.43	25.9	49.17	+0.48	-0.99	+51 2.17	+0.46
"	25	8.54	26.2	57.37	+0.63	-0.91	7.87	+0.44
March	5	8.03	26.4	+50 2.23	+0.61	-1.00	6.73	-0.14
"	25	7.94	26.6	16.72	+0.72	-0.92	10.72	+0.20
Apr.	21	8.22	26.6	36.74	+0.74	-0.90	1.24	-0.35
June	27	8.20	24.1	50.70	+0.21	-0.82	+50 57.70	-0.05
Sept.	1	8.66	21.0	29.38	-0.32	-0.57	29.38	-0.43
"	3	8.64	22.6	29.36	-0.01	-0.65	28.86	-0.26
"	7	8.35	22.6	28.35	-0.25	-0.90	24.35	-1.13
Oct.	19	8.05	24.0	33.86	+0.13	-0.86	1.86	-0.54
"	31	7.99	25.2	37.20	+0.28	-1.03	+49 53.70	-0.68
Nov.	4	8.32	25.1	40.33	+0.78	-0.50	52.53	-0.29
"	22	8.39	26.1	51.46	+0.62	-0.91	39.96	-0.70
Dec.	6	8.18	26.3	+51 2.09	+0.76	-0.82	31.09	-0.63
"	16	8.20	25.6	9.58	+0.75	-0.65	23.58	-0.75
1906 Jan.	8	8.24	26.2	26.52	+0.74	-0.81	9.02	-0.63
Febr.	24	8.45	26.3	+52 8.84	+0.90	-0.68	+48 11.34	-1.23
March	11	8.37	27.3	26.09	+1.15	-0.67	+47 58.09	-0.88
"	21	8.11	26.7	33.93	+0.78	-0.90	48.43	-0.97
Apr.	3	7.90	26.6	43.32	+0.72	-0.92	35.62	-0.99
May	6	8.45	25.8	58.36	+0.46	-1.00	0.96	-1.05
June	1	8.14	24.2	52.20	-0.24	-1.28	+46 29.84	-1.21
"	18	8.09	22.7	39.07	-0.77	-1.43	1.57	-1.66
July	19	8.52	20.8	8.52	-0.98	-1.22	+45 9.52	-1.68

II. *Time determinations at Chiloango. Corrections and rates of the chronometers.*

In 1903 before I left for Africa I added to my chronometer of HEWITT another of HOHWÜ. During my stay at Chiloango from May 1903 to July 1906 I have regularly controlled both by making at proper intervals time determinations in the same way as before by altitudes determined with my altazimuth. Moreover I have daily intercompared the two chronometers.

With regard to the time determinations themselves I need only add to what has been said before :

1. that new determinations of the value of a level-part yielded 5".4, exactly as before;

2. that the flexure and the division errors of the instrument were regularly taken into account according to the formulæ in "*Contributions I*".

Here follow the results for the corrections and rates of the chronometers. The rates, and also the temperatures added to them, refer to the interval between the date on one line above and that on the line itself. The temperatures for the periods of the two journeys are wanting. To the "*Rates HEWITT 20° C.*" I shall refer later.

I have first investigated the rates of the chronometers with regard to the temperature and to this end I have formed mean rates for periods of about 2 months, in each summer and winter.

Period	Temp. C.	Chron. Hewitt.	Chron. Hohwü.
1903 June 20—Aug. 4	19.63	— 1 05 ^s	— 0 73 ^s
Nov. 5—March 31 ¹⁾	25.58	+ 0 71 ^s	+ 0 59 ^s
1904 June 24—Sept. 30	21.03	— 0.24	+ 0.34
1905 Febr. 12—April 21	26.42	+ 0.70	— 0.01
June 27—Sept. 1	20.95	— 0.32	— 0.43
1906 Jan. 8—April 3	26.83	+ 0.90	— 1.10
June 18—July 19	20.82	— 0.98	— 1.68

For the chronometer of HEWITT I found a very distinct influence of the temperature and, in so far as I could find then, no variation with time.

¹⁾ I have excluded the period of my journey from Dec. 20 to Jan. 3.

For the simple means of the 4 winter and the 3 summer rates and of the temperatures belonging to them I find:

$$26^{\circ}.28 \quad + \quad 0^{\text{s}}.77$$

$$20.61 \quad - \quad 0.65$$

hence: Variation per degree $+ 0^{\text{s}}.25$ ¹⁾

By means of this coefficient of temperature I have reduced all the rates to 20° ; these reduced rates are given in the table above in the column: D. Rate 20° C. The simple mean value of these reduced rates is $- 0^{\text{s}}.87$, from which the real mean reduced rate $- 0^{\text{s}}.83$ differs only little. By forming the differences between the reduced rates and their mean I found for the mean error of a daily rate, disregarding the different lengths of the intervals between the time determinations:

$$\text{M.E.} \pm 0^{\text{s}}.225$$

a very satisfactory result, especially in consideration of the fact that for the whole period of more than 3 years we have adopted a constant rate depending on the temperature only.

For the chronometer of HOHWÜ the results are somewhat less favourable. One sees at a glance a distinct variation with time which from 1904 seems to continue in the same sense.

In order to derive the coefficient of temperature I have compared each summer rate with the mean of the two neighbouring winter rates and thus found:

$$\text{Rate summer—winter} \quad + \quad 0^{\text{s}}.78$$

$$\quad + \quad 0.03$$

$$\quad - \quad 0.05$$

A regular influence of the temperature does not appear from these data and the greater value of the first difference must be ascribed to an irregular variation in the beginning. Therefore I have accepted for the coefficient of temperature $0^{\text{s}}.00$ and, in order to investigate the variation which is independent of the temperature I have formed mean rates for periods of about three months. They follow here together with the corresponding values for the chronometer of HEWITT reduced to 20° .

¹⁾ It was impossible to determine also a quadratic term on account of the small differences of temperature. For the years 1901—'02 the temperature coefficient was found to be $+ 0^{\text{s}}.18$.

DAILY RATES FROM PERIODS OF THREE MONTHS.

	D. Rate Hewitt red. to 20°	D. Rate Hohwü
	^s	^s
1903 May 15—Aug. 4	— 1.08	— 0.49
Aug. 4—Nov. 5	— 0.90	+ 0.07
Nov. 5—Jan. 29	— 0.86	+ 0.65
1904 Jan. 29—May 12	— 0.51	+ 0.55
May 12—Aug. 1	— 0.56	+ 0.72
Aug. 1—Nov. 5	— 0.66	+ 0.34
Nov. 5—Jan. 21	— 0.93	+ 0.91
1905 Jan. 21—Apr. 21	— 0.94	+ 0.10
Apr. 21—June 27	— 0.82	— 0.05
June 27—Nov. 4	— 0.72	— 0.50
Nov. 4—Febr. 24	— 0.76	— 0.90
1906 Febr. 24—May 6	— 0.90	— 0.99
May 6—July 19	— 1.29	— 1.51

The values of this table also show the greater regularity of the chronometer of HEWITT for which only the last rate shows a greater deviation. The rate of that of HOHWÜ seems tolerably constant during the period 1903 Nov. 5—1905 Jan. 21 for which the mean rate amounts to + 0^s.61.

From the differences between the single rates in this period and their mean we find, again disregarding the lengths of the intervals:

$$\text{M.E. Daily rate HOHWÜ} \pm 0^s.30$$

still greater than for HEWITT. But on the other hand the large coefficient of temperature of the latter is a disadvantage for periods for which the temperature is not accurately known.

III. *New determination of the latitude of Chiloango.*

In the months of November and December 1903 I made a new determination of the latitude of Chiloango, again by altitudes observed with my universal instrument, with the only difference that a much greater number of stars was observed, but with only one pointing for each of them at the moment of transit over the meridian. The observations were arranged so that 2 northern and 2 southern stars

1903 DECEMBER 7

Adopted runcorrection for 10' — 0".66
 " zenith point 239°59'47".32
 Temperature and barometer for 1st star 25.3 759.4
 4th " 24.9 759.5
 6th " 24.6 759.6
 12th " 24.0 759.8

Star		Readings		Level corr.	Zenithdist.	Refr.	Lat.
		Micr. A	Micr. B				
α Sculptoris	R	264°40' 15"	39' 51"	— 3'.89	24°40' 12".12	25".37	—5°11'
		45	51				68".01
β Phoenicis	L	197 58 49	58 24	— 2.97	42 1 14.53	49.73	69.94
		48	23				
β Andromedae	R	280 18 7	17 42	0.00	40 18 8.23	46.82	64.95
		7	47				
δ Cassiopeiae	L	175 5 24	5 5	+ 2.59	64 54 31.00	1' 57.47	65.87
		23	3				
γ Phoenicis	R	278 35 57	35 33	+ 1.08	38 35 58.96	44.13	67.91
		58	33				
α Eridani	L	187 29 33	29 15	— 2.43	52 30 26.79	1 12.04	66.67
		34	41				
φ Persei	R	295 23 16	22 57	— 3.78	55 23 14.28	1 20.03	66.71
		12	56				
ε Cassiopeiae	L	171 38 9	37 56	+ 0.54	68 21 44.73	2 18.50	62.93
		9	55				
α Hydri	R	296 49 0	48 39	+ 0.81	56 49 1.24	1 24.44	65.02
		48 58	35				
γ Andromedae	L	192 56 47	56 23	— 4.86	47 3 18.03	59.55	62.48
		45	22				
α Arietis	R	268 12 3	41 38	— 1.62	28 12 2.27	29.75	59.02
		5	38				
φ Eridani	L	193 15 24	14 55	+ 2.70	46 44 35.38	58.91	64.91
		22	56				

Date	Star		Zenith dist.	Latitude			
				N. R.	N. L.	S. R.	S. L.
1903				— 5°11'			
November 28	α Toucani	R	S 60°			57''42	
Zenithp. 180°	α Phoenicis	L	S 38				58''21
	α Cassiop.	R	N 61	66''43			
	γ Cassiop.	L	N 65		71''99		
	α Sculptoris	R	S 25			49.73	
	β Phoenicis	L	S 42				59.27
	β Androm.	R	N 40	65.53			
	ν Piscium	L	N 32		71.42		
	δ Cassiop.	R	N 65	67.73			
	Mean			66.56	71.70	53.58	58.74
December 2	γ Cassiop.	L	N 65		67.85		
Zenithp. 210°	α Sculptoris	R	S 25			57.91	
	β Androm.	R	N 40	67.85			
	Mean			67.85	67.85	57.91	
December 6	α Sculptoris	R	S 25			60.98	
Zenithp. 210°	β Phoenicis	L	S 42				64.35
	β Androm.	R	N 40	69.94			
	δ Cassiop.	L	N 65		69.59		
	γ Phoenicis	R	S 39			63.53	
	α Eridani	L	S 53				59.45
	Mean			69.94	69.59	62.26	61.90
December 7	α Sculptoris	R	S 25			68.01	
Zenithp. 240°	β Phoenicis	L	S 42				69.94
	β Androm.	R	N 40	64.95			
	δ Cassiop.	L	N 65		65.87		
	γ Phoenicis	R	S 39			67.91	
	α Eridani	L	S 53				66.67
	φ Persei	R	N 55	66.71			
	ε Cassiop.	L	N 68		62.93		

Date	Star		Zenith dist	Latitude			
				N. R.	N. L.	S. R.	S. L.
				— 5° 11'			
Dec. 7 cont.	α Hydri	R	S 57°			65°02	
	γ Androm.	L	N 47		62°48		
	α Arietis	R	N 28	59°02			
	φ Eridani	L	S 47				64°91
	Mean			63.56	63.76	66.98	67.17
December 10	δ Cassiop.	L	N 65		63.11		
Zenithp. 270°	γ Phoenicis	R	S 39			68.08	
	α Eridani	L	S 53				69.66
	φ Persei	R	N 55	61.18			
	ε Cassiop.	L	N 68		64.79		
	α Hydri	R	S 57			68.58	
	β Trianguli	R	N 40	62.54			
	φ Eridani	L	S 47				71.22
	Mean			61.86	63.95	68.33	70.44
December 14	γ Phoenicis	R	S 39			62.22	
Zenithp. 300	α Eridani	L	S 53				62.88
	β Arietis	R	N 26	58.41			
	α Hydri	R	S 57			65.99	
	γ Androm.	L	N 47		59.56		
	β Trianguli	R	N 40	64.07			
	φ Eridani	L	S 47				61.99
	δ Hydri	R	S 64			64.13	
	Mean			61.24	59.56	64.11	62.44
December 15	δ Cassiop.	L	N 65		68.96		
Zenithp. 330	γ Phoenicis	R	S 39			64.05	
	α Eridani	L	S 53				59.03
	φ Persei	R	N 55	72.49			
	ε Cassiop.	L	N 68		68.16		
	α Hydri	R	S 57			57.46	
	γ Androm.	R	N 47	67.16			
	β Trianguli	L	N 40		68.18		
	φ Eridani	L	S 47				59.67
	Mean			69.82	68.43	60.76	59.35

were observed alternately, and of each of these pairs the one in the position circle to the right, the other in the position circle to the left.

The readings were always made with each of the two microscopes both on the preceding and on the following division. The corrections for run and for the level reading were applied exactly as before (comp. *Contrib.* I. p. 280), the refraction was derived from the tables of BESSEL and the declinations of the stars were taken as before from the *Nautical Almanac*, i. e. from the catalogue of NEWCOMB. Only now and then I have also observed stars from the *Berliner Jahrbuch*, namely ν Piscium, δ Cassiopeiae and φ Persei. To reduce them to NEWCOMB I have applied to them the following corrections: $-0''.1$, $-0''.8$ and $+0''.7$, according to data communicated to me by Dr. E. F. v. D. SANDE BAKHUYZEN.

The reading for the zenith was assumed to be constant for each night and determined so as to make all the stars agree inter se as well as possible. By the regular alternation of the positions of the instrument an error in the adopted zenith point was eliminated almost entirely.

The observations were made in 6 positions of the circle, each differing from the next by 30° .

As an example I will first give the observations of one night in full.

I now proceed to give for all the observations the resulting values for the latitude in 4 columns: for the north stars circle right and left and for the south stars circle right and left. To these I add the approximate zenith distances of the stars.

The observations at zenith point 210° are distributed over two nights, Dec. 2 and Dec. 6. Because it is not permissible to consider the zenith point for the two as exactly equal, it seemed better to exclude from the observations of Dec. 2 the only southern star obtained. For the rest no observations are excluded, not even the few which deviated rather much.

For each position of the circle I have combined the results for the two positions of the instrument, but I kept apart those from the northern and from the southern stars and so I obtained: (see p. 100)

To the results from the northern and the southern stars I have added their differences and their means. In so far as we may assume that the north and the south stars had in the mean the same zenith distance, the former represent the corrections to the measured arcs of $2z$ for errors of division $+$ double the correction to the measured z for flexure (comp. *Contrib.* I p. 285), while on the

Zenithpoint	North stars	South stars	N-S	$\frac{N+S}{2}$
	- 5° 11'			- 5° 12'
180°	69.13	56.16	- 12.97	2.64
210	68.81	62.08	- 6.73	5.44
240	63.66	67.08	+ 3.42	5.37
270	62.90	69.38	+ 6.48	6.14
300	60.49	63.28	+ 2.88	1.84
330	69.12	60.06	- 9.06	4.59
Mean	65.67	63.01	- 2.66	4.34

same supposition the means from the north and the south stars are free from these two errors.

To derive the errors of division and of flexure we obtain, the mean zenith distance amounting to 49° , with the same notations as before :

$$a' = 2a \sin 98^\circ = - 10.''16$$

$$b' = - 2b \sin 98^\circ = + 0.83$$

$$c' = 2c \sin 49^\circ = - 2.66$$

whence, if α stands again for the circle reading :

$$\begin{aligned} \text{Correction for division errors to the circle reading} &= -5.''13 \sin 2\alpha - 0.''41 \cos 2\alpha \\ &= +5.''15 \sin (2\alpha - 175.^\circ 4) \end{aligned}$$

$$\text{Correction for flexure to the zenith distance} = -1.''76 \sin z.$$

The mean of the values in the last column is :

$$\varphi = - 5^\circ 12' 4''.34.$$

The formula for the correction for division errors agrees very well with that derived from the observations of 1900—01, which is of importance for the correction of my other observations of zenith distances. For the coefficient of the flexure I had formerly found $-0.''60$; the difference may still be ascribed to accidental causes.

Finally I give here the 12 separate results for the latitude, each corrected for division errors and flexure. (see p. 101).

Their mean value must of course be equal to that of the uncorrected results. From the comparison of the former with their mean we derive for the mean error of the final result $\pm 0.''57$. Hence this is :

$$\varphi = - 5^\circ 12' 4''.34 \pm 0.''57.$$

The observations were made in the factory of the firm HATTON and COOKSON.

Determination of the longitude. A time determination of 26 Dec. by means of 4 observations of β Orionis in both positions of the instrument, each time over 7 horizontal threads, yielded the following corrections of the chronometers to the mean time of N'Kutu. Together with these I give the corrections to the mean time of Chiloango derived by simple interpolation — the best thing to be done — between the time determinations of Dec. 20 and Jan. 3, and finally the resulting difference of longitude.

December 26.296 (M. T. Chiloango).

	Hohwü	Hewitt
Correction to M. T. N'Kutu	+ 48 ^m 48 ^s .85	+ 49 ^m 22 ^s .35
„ „ „ Chiloango	46 50 .29	47 22 .27
Difference of longitude	— 1 58 .56	— 1 60 .08

Adopting the simple mean of the two results, we find for the longitude of N'Kutu relatively to Chiloango

$$- 1^m 59^s.32.$$

Determination of the latitude. On December 29 I secured a determination of the latitude by 3 pairs of observed zenith distances, i.e. three observations in each position of the instrument, of β Andromedae ($z = 40^\circ$ North) and by 2 pairs of α Eridani ($z = 53^\circ$ South).

The results were :

β Andromedae	1 st pair	— 4°57' 9".90
	2 ^d „	11.06
	3 ^d „	11.24
	Mean	10.73
	Corrected	— 4°57' 5".74
α Eridani	1 st pair	— 4°56'57".69
	2 ^d „	59.81
	Mean	58.75
	Corrected	— 4°57' 3".72

Hence the mean result for the latitude is :

$$- 4^\circ 57' 4".7$$

2. *Journey of 1904 June 2—23. Corrections of the chronometers.*

As this journey was made almost entirely by land the circumstances were much less favourable for the regularity of the chronometers, in spite of all precautions taken. The intercomparisons, which were made at least once every day, clearly show small irregularities now and then and once on June 3, when the carriers were not yet accustomed to their task, as I have said before, a serious perturbation occurred.

The instruments were almost always carried in the shadow of the woods and only a few times they can have been exposed to the sunbeams. We must assume, however, that they were subject to the general fall of temperature which occurs in these parts in June, and thence follows that we may not accept a constant rate for the chronometer of HEWITT.

From my regular thermometer readings in 1903 and 1905 I derive for the mean fall of temperature during June $2^{\circ}.18$, i. e. on an average per day $0^{\circ}.073$; this would cause a variation of rate for HEWITT of $-0^{\circ}.018$ per day. On this supposition and starting from the time determinations at Chiloango of May 30 and June 24, the daily rate would have been at the beginning (May 30—31) $+0^{\circ}.50$ and at the end (June 23—24) $+0^{\circ}.08$.

As the temperature coefficient of HOHWÜ may be considered zero, we may gather some evidence on this point from the relative rates during the journey. Beginning after the perturbation on June 3, I find the following differences between the two chronometers, each being the mean result from at least three comparisons, and derive from them the relative rates subjoined.

		Hohwü — Hewitt	
June	5	+ 49. ^s 00	— 0. ^s 37
	10	47. 17	— 0. 53
	15	44. 50	— 1. 07
	20	39. 17	— 0. 92
	24	35. 50	

As the mean rate of HOHWÜ was about $+0^{\circ}.9$, these values agree fairly well with the assumed variable rate for HEWITT, which I therefore adopt as the most probable. For the middle of the period, June 12, the chronometer correction derived by means of the latter rates differs from that which would follow from the constant rate $+0^{\circ}.29$ by $1^{\circ}.36$.

A great difficulty is caused by the perturbation on June 3, when the difference between the chronometers seems to have varied abruptly

3 secs. It was probable that this must be attributed to the chronometer HOHWÜ, which supposition seems confirmed by the time determination at N'Kutu of June 5 if we reduce it to Chiloango with the difference of longitude determined in Dec. 1903, but it is undoubtable that we have here a source of uncertainty for the following determinations of longitude. I already remark here that I have finally accepted no jump in HEWITT and one of 2 seconds in HOHWÜ. For the daily rate of the latter we then must accept $+0^s.91$ instead of $+0^s.83$. In addition I remark that also for the determinations in 1904 I have assigned equal weights to the two chronometers.

3. Determinations of longitude in 1904.

Mayili. On June 2 I here secured a time determination by means of Sirius west, and of α Bootis east of the meridian. The results obtained from the two, corrected for division errors and flexure, differ inter se by $0^s.37$.

Here follow the mean results, to which I have added the corrections to the mean time of Chiloango derived by means of the adopted rates ($+0^s.91$ for HOHWÜ and a variable rate for HEWITT) and the difference of longitude derived thence.

June 2 6 ^h 5 M.T. Chiloango		
	Hohwü	Hewitt
Correction to M.T. Mayili	$+ 49^m50^s.89$	$+ 50^m36^s.39$
" " " Chiloango	$+ 48 29 .33$	$+ 49 17 .08$
Difference of longitude	$- 1 21 .56$	$- 1 19 .31$
	Mean	$- 1^m20^s.44$

In 1902 I had found $- 1^m21^s.3$.

If we had derived the correction of HOHWÜ with a rate of $+0^s.83$, the difference of longitude according to this chronometer would have been $- 1^m21^s.80$, while HEWITT with an assumed constant rate would have yielded $- 1^m19^s.89$.

N'Kutu. Here I was obliged to have recourse to the sun for determination of time and on June 5 I obtained the following results from 4 observations of the two limbs in the two positions of the instrument. I now begin by deriving the correction of HOHWÜ to the M. T. of Chiloango, without accepting a jump, and therefore with the rate $+0^s.83$.

June 5 3^b.1 M.T.

	Hohwü	HEWITT
Correction to M.T. N'Kutu	+ 50 ^m 28 ^s .54	+ 51 ^m 17 ^s .54
" " " Chiloango	+ 48 31.45	+ 49 18.30
Difference of longitude	— 1 57.09	— 1 59.24

while the result of Dec. 1903 was — 1^m59^s.32. From this it would appear that on June 3 a perturbation occurred in Hohwü and not in HEWITT and that the jump in the former amounts to about 2 secs., which agrees sufficiently with the observed abrupt variation in the difference between the two.

For a more accurate investigation of the perturbation I have tried to avail myself of the time determination of June 2 at Mayili, after having reduced it to Chiloango by means of the difference of longitude determined in 1902, but this has not thrown more light on the subject. Everything considered I have finally accepted as the effect of the perturbation: a jump of 2 seconds in Hohwü.

As to the longitude of N'Kutu itself, it will be best to use for it only the determination of Dec. 1903, although the new determination by HEWITT perfectly agrees with it.

Buku-Zan. My observations were made in the factory of the firm HATTON and COOKSON. For a time determination I could obtain only 3 pointings at the sun's limbs on June 14. To their results I have added the corrections to M. T. Chiloango according to the adopted computation (i. e. with a jump in Hohwü and a variable rate of HEWITT) and also the difference of longitude derived from them.

June 14 4^b0 M.T.

	Hohwü	HEWITT
Correction to M.T. Buku-Zan	+ 50 ^m 13 ^s .43	+ 50 ^m 57 ^s .93
" " " Chiloango	+ 48 38.12	+ 49 21.22
Difference of longitude	— 1 35.31	— 1 36.71
Mean	— 1 ^m 36 ^s .01	

Computed with constant rates and without an assumed jump the results would have been — 1^m34^s.51 and — 1^m38^s.02, hence in less good harmony.

Chimbete. Also here (factory of HATTON and COOKSON) I could observe only the sun for a time determination, but I secured at least a complete set of 4 observations of both limbs in both positions; the two pairs computed separately differ by 0.^s83.

The results were the following; to these I have added the corrections to M. T. Chiloango according to the adopted computations, and the difference of longitude derived by means of them.

June 21 3^h6 M. T.

	HOWÜ	HEWITT
Correction to M. T. Chimbete	+ 50 ^m 37 ^s 73	+ 51 ^m 15 ^s 73
" " " Chiloango	+ 48 44.46	+ 49 22.52
Difference of longitude	— 1 53.27	— 1 53.21
Mean	— 1 ^m 53 ^s 24	

whereas if computed with constant rates without an assumed jump I would have got — 1^m53^s03 and — 1^m53^s81.

Thus the results following from the two computations differ much less than for the other places.

4. Determinations of latitude in 1904.

Buku-Zan. For a determination of the latitude I could observe only on June 15 one star in the south, β Centauri. Of this star I obtained 8 pointings distributed equally over the two positions.

The results were :

1 st pair $\varphi =$	— 4° 46' 4"46
2 nd " "	5.51
3 rd " "	8.54
4 th " "	6.51
Mean	6.26

and after correction for division error and flexure

$$\varphi = - 4^{\circ} 46' 11'' .1.$$

Chimbete. I only succeeded on June 20 in securing 10 pointings on α Crucis, distributed equally over the two positions, with the following results.

1 st pair $\varphi =$	— 5° 1' 18"40
2 nd " "	18.65
3 rd " "	21.83
4 th " "	20.53
5 th " "	19.52
Mean	19.78

and after correction for division error and flexure

$$\varphi = - 5^{\circ} 1' 24'' .5$$

5. Final results.

I finally accept the following values as the most probable results of my determinations of the longitude and the latitude of the four stations in the interior. For the longitude of Mayili I take the mean of the two determinations and for that of N'Kutu I use only that of 1903.

	Latitude	Difference of longitude with Chiloango
Mayili	— 5° 4' 40"	— 1 ^m 20 ^s .9
N'Kutu	— 4 57 5	— 1 59.3
Buku Zan	— 4 46 11	— 1 36.0
Chimbete	— 5 1 25	— 1 53.2

Astronomy. — “*Contributions to the determination of geographical positions on the West-coast of Africa. III. Appendix.*” By C. SANDERS. (Communicated by E. F. VAN DE SANDE BAKHUYZEN).

6. *Modified computation of the determinations of longitude in 1904.*

For the computation of the corrections of my chronometers to the M. T. of Chiloango during my journey of June 1904 I have supposed that the chronometer of HEWITT had not been influenced by the perturbation on June 3 and that the one of HOHWÜ had advanced 2 secs.

I had adopted the value of 2 secs. chiefly in order not to exaggerate. But the result of the time determination on June 5 at N’Kutu, taking into account the modification of the rate involved in the supposition of a jump of a given amount, as well as the comparisons on June 3 render it more probable that HOHWÜ advanced 3 secs.

I shall therefore give here the results which we obtain on the latter supposition, assuming a daily rate for HOHWÜ of $+0^s.95$. I shall also show to what results we should arrive if we adopted the extreme supposition in the opposite sense, namely that HOHWÜ was not perturbed and that HEWITT had omitted 6 beats = 3 secs, and if we again assumed daily rates of both in accordance with the last supposition. This supposition is not very probable but neither quite impossible, and in this way we may at least form some idea of the still remaining uncertainty. For the rest I still hold the supposition that the rate of HEWITT has varied during the journey owing to the fall of temperature. Here follow the values obtained for the difference of longitude between the 4 stations and Chiloango:

a on the previous supposition ;

b adopting for HOHWÜ a jump of 3 secs. ;

c adopting a jump of 3 secs. in the opposite sense for HEWITT.

		HOHWÜ	HEWITT	MEAN
Mayili	<i>a</i>	— 1 ^m 21 ^s 56	19 ^s 31	— 1 ^m 20 ^s 44
	<i>b</i>	21.45	19.31	20.38
	<i>c</i>	21.80	19.66	20.73
N’Kutu	<i>a</i>	— 1 ^m 58 ^s 62	59 ^s 24	— 1 ^m 58 ^s 93
	<i>b</i>	59.39	59.24	59.32
	<i>c</i>	57.09	56.94	57.02
Buku Zan	<i>a</i>	— 1 ^m 35 ^s 31	36 ^s 71	— 1 ^m 36 ^s 01
	<i>b</i>	35.73	36.71	36.22
	<i>c</i>	34.51	35.49	35.00

		HÖHWÜ	HEWITT	MEAN
Chimbete	<i>a</i>	— 1 ^m 53 ^s 27	53 ^s 21	— 1 ^m 53 ^s 24
	<i>b</i>	53.41	53.21	53.31
	<i>c</i>	53.03	52.83	52.93

We find in the first place that the longitude of N'Kutu on supposition *b* agrees exactly with the result of December 1903 which was 59^s.32, and on supposition *c* differs strongly from it, whence appears clearly that the latter is less probable. It further appears that, with regard to the three other stations, the results on the two extreme suppositions *b* and *c* differ 1^s.2 for Buku Zan and only 0^s.4 for Mayili and Chimbete, while the results on suppositions *a* and *b* differ for Buku Zan 0^s.2 and for Mayili and Chimbete less than 0^s.1. The results from the two chronometers separately accord fairly well inter se, Mayili excepted.

As we reject the result of 1904 for N'Kutu and replace it by that of 1903 and as for Mayili we can take the mean of the results of 1902 and 1904, we find that the uncertainty caused in the final results by the perturbation is less than was to be feared.

Lastly I give here the final results obtained in this way, assuming thereby the most probable supposition *b*:

Difference of longitude with Chiloango

Mayili	— 1 ^m 20 ^s .8
N'Kutu	— 1 59.3
Buku Zan	— 1 36.2
Chimbete	— 1 53.3

The differences with the values adopted before are at the utmost 0^s.2.

Astronomy. — “*Observation of the transit of Mercury on November 14, 1907 at Chiloango in Portuguese West-Africa*”. By C. SANDERS. (Communicated by Dr. E. F. VAN DE SANDE BAKHUYZEN).

(Communicated in the meeting of May 30, 1908).

For a short time I have possessed a telescope of ZEISS of 80 mm. aperture and 120 cm. focal length. With this telescope I intend to observe in the first place occultations of stars in order to determine the longitude of my observing station with greater precision than hitherto has been possible. For the present the telescope has an azimuthal mounting, which however soon will be replaced by an equatorial mounting with slow motions and small divided circles. In the mean time

I have been able to use the telescope for observing, at least partly, the transit of Mercury on November 14 1907, and I venture to publish my results here.

To give my telescope a firm basis I had a pier built of beton surrounded by an isolated floor and provided with a movable roof open at the sides, which roof can be entirely moved aside. For the transit of Mercury, however, I kept the roof over the instrument in order to protect myself from the burning sunbeams and especially to keep out the light from outside as much as possible.

For the observations I had constructed a projection apparatus, a kind of camera having the shape of a truncated pyramid, of which one side is open and the three others are coated with black paper. The base on which the image was to be formed was at a distance of about 14 cm. from the eye piece. The camera was adjustable in distance and in inclination, to secure the proper position of the plane of the image.

With the highest power of the telescope, 133, the diameter of the projected image of Mercury was nearly 1 mm. The fine solar spots that were present could be sharply observed and those in the neighbourhood of the western limb could be seen surrounded by very distinct faculae.

Unfortunately the beginning of the transit was hidden from my view by clouds. Towards 1 o'clock mean time of Chiloango it began to clear up and, after Mercury had been visible on the sun as a well defined disc, its egress could be observed very well. I found:

third contact at 2^h35^m38^s M.T. Chiloango
last ,, ,, 2 38 7 ,, ,,

The moment of the 4th contact, that at which the last impression on the limb seemed to disappear, was difficult to estimate within some seconds chiefly owing to the unsteadiness of the images, but I hold that but for this unsteadiness the observation of the last internal contact could have been made with great precision. The corrections of my chronometers were derived from time determinations before and after the transit.

The times computed from the Nautical Almanac for the 3rd and the 4th contact at Chiloango were 2^h35^m47^s and 2^h38^m24^s. Thence follow for the differences observation — computation: — 9^s and — 17^s.¹⁾

¹⁾ (Note added by E. F. v. D. SANDE BAKHUYZEN). According to the mean of the observations made at Leiden, these differences were —6^s and —21^s. Hence the results of Mr. SANDERS agree very well with these. The greater difference for the 4th contact must probably be ascribed to the circumstance that all the observers have observed this phenomenon too early.

Zoology. — “*Some results of the investigation of the Cirripeds collected during the cruise of the Dutch man-of-war “Siboga” in the Malay Archipelago.*” By Dr. P. P. C. HOEK.

Having explained the position the Cirripeds occupy in the Class Crustacea the author emphasized first of all the great advantage of possessing DARWIN'S well-known Monograph ¹⁾ when studying the animals of this group. This book may still be considered as a model for similar monographs, not only in treating the Sub-Class from a general point of view, but also for the description of the different species.

As might be expected the study of the material collected with the “Siboga” has considerably increased our knowledge concerning the biology, the mutual relations and the anatomy of these animals: a few interesting cases have already been communicated to the Academy²⁾ and a more detailed treatment is given in the Report on the group published in the Results of the Expeditions edited by Prof. MAX WEBER. The first part of this Report on the Cirripeds was published in September 1907, a great deal of the second part and the determination of nearly the whole material has been achieved by this time.

To have an idea of the importance of the material collected by the “Siboga” it is worth while to compare it with that obtained during the English expedition with the “Challenger”. The English man-of-war the “Challenger” made a cruise round the world, which lasted about three years and a half, and brought home collections from nearly all the oceans and seas of the earth's surface; the Cirripeds collected during that cruise were also worked up by the present author, the report on the group was published in 1883. From the accompanying table it may now be seen that the material collected by the “Siboga” in the course of one year, and, comparatively speaking, in an area of limited extension, is not inferior to that of the “Challenger”; the latter, however, collected the greater part of its spoil from the bottom of the great oceans of the world where as a rule the depth was very important. The “Siboga” on the other hand, had better opportunity to investigate coasts, reefs etc. Hence it is easily understood that whereas the “Challenger” from depths to over 5000 m. obtained a richer collection of true deep-sea-animals, the “Siboga” succeeded in collecting along with an

¹⁾ DARWIN, CH., Monograph of the Subclass Cirripedia (in 2 Volumes). Vol. I. The Lepadidae or Pedunculated Cirripedes, 1851; Vol. II. The Balanidae (or Sessile Cirripedes); The Verrucidae etc. 1854. London: Printed for the Ray Society.

²⁾ Proceedings of the Academy of Sc. of June 25th, 1904 and January 27th, 1906.

COMPARISON OF THE CIRRIPEDS COLLECTED BY THE "SIBOGA",
WITH THOSE OBTAINED BY THE "CHALLENGER".

Genera	Siboga: Malay Archipelago				Challenger: Voyage round the world			
	Number of species collected	Of these were novae species	Of these were collected at depths from 200—499 m.	Idem from 500—2800 m.	Number of species collected	Of these were novae species	Of these were collected at depths from 200—499 m.	Idem from 500—5130 m.
<i>Lepas</i>	2	—	—	—	6	—	—	—
<i>Poecilasma</i>	7	3	3	—	2	2	—	2 ⁵⁾
<i>Dichelaspis</i>	5	4	—	1 ¹⁾	1	1	—	1 ⁶⁾
<i>Conchoderma</i>	—	—	—	—	2	—	—	—
<i>Megalasma</i>	2	1	1	—	1	1	—	—
<i>Alepas</i>	5	5	1	2 ²⁾	1	1	—	1 ⁷⁾
<i>Microlepas</i> n. gen.	1	1	—	—	—	—	—	—
<i>Ibla</i>	2	1	—	—	—	—	—	—
<i>Scalpellum</i>	38	32	8	22	43	43	7	36
<i>Pollicipes</i>	1	—	—	—	—	—	—	—
<i>Lithotrya</i>	4	1	—	—	—	—	—	—
<i>Balanus</i>	±20*)	±10*)	3	1 ³⁾	40	5	2	1 ⁸⁾
<i>Acasta</i>	2	1	—	—	1	—	—	—
<i>Tetraclita</i>	3	—	—	—	2	—	—	—
<i>Pyrgoma</i>	3	2	1	—	—	—	—	—
<i>Creusia</i>	1	—	—	—	—	—	—	—
<i>Coronula</i>	—	—	—	—	1	—	—	—
<i>Chthamalus</i>	2	—	—	—	2	1	—	—
<i>Hexelasma</i> n. gen.	1	1	—	1 ⁴⁾	—	—	—	—
<i>Verruca</i>	7	6	—	6	6	6	—	6
Total	106	68	17	33	78	60	9	47

50 deepsea-spec.

56 deepsea-spec.

*) Provisional determination.

1) *Dichelaspis Weberi* from a depth of 560 m.2) *Alepas morula* from 538 m. and *Alepas ovalis* from 984 m.3) *Balanus alatus* from 564 m.4) *Hexelasma arafurae* from 560 m.5) *Poecilasma carinatum* from 750 m. and *P. gracile* from 740 m.6) *Dichelaspis sessilis* from 1800 m.7) *Alepas pedunculata* from 740 m.8) *Balanus hirsutus* from 900 m.

important deepsea-material, a greater number of shallow-water forms: a richer collection altogether, as many species of Cirripeds belong to the coastal fauna.

However, this table was not compiled especially to show the greater number of species collected by the Dutch expedition. Its main object is to point out that the deepsea-material of all the oceans and seas of the world together, as far as Cirripeds are concerned, has after all no other composition than that which was collected in a relatively small area, the Malay Archipelago. For both collections that composition comes to this, that after all only two genera *Scalpellum* and *Verruca*, in deeper water, are represented by numerous species and that the other genera which do occur in that deeper water are represented there by very few forms only. It is true that the genera *Scalpellum* and *Verruca*, in shallow water, are also represented by several species: we now know 125 species of *Scalpellum*, which are so-called "good" species and which in any case, almost without exception, can easily be distinguished from one another; of these 90 live at depths of over 500 m. to ca. 5000 m. and 35 in shallower water. The number of known species of *Verruca* now amounts to 36; of these 5 were observed in shallow water and 31 at depths from 500 to ca. 3400 m. In deep water, however, only these two genera found circumstances specially favourable for the formation of new species, whereas the same for other genera holds good in more shallow water. As an instance of the latter the genus *Balanus* may be pointed out: of this genus by this time over 60 species are known and, therefore, it can safely be considered as one rich in species. However, only 5 of these have been observed in water of a depth of 200—500 m. and of the latter only 2 at a depth down to 564 m. On the other hand 55 species of this genus are known, which inhabit the coast or relatively shallow water only.

The author thinks that at the present moment our knowledge is by far too incomplete to permit of an explanation of phenomena of this kind; in such cases all we can do is to try to state and to control the facts as accurately as possible and we must then confine ourselves to considering it as a peculiarity of a few genera that their numerous species divide themselves over so strongly divergent depths, whereas it is characteristic of other genera that none, or a single, or a few species only have been able to adapt themselves to somewhat more considerable depths.

It is remarkable at the same time, and this holds good for the genus *Scalpellum* especially, but for most of the known species of *Verruca* also, that such richness in species is accompanied by so great

an isolation of the different forms. Of course, we cannot express our opinion on this matter with absolute certainty, as dredging, especially in deeper water, always remains an insecure method of testing the greater or lesser commonness of a species at the place where it occurs. Yet it is very striking, that in the collections made the species of Cirripeds from deeper water nearly without an exception are represented by one or by a very few specimens only. Especially when taking into consideration that the pelagic Cirripeds and those living near the coast or in shallow water, are nearly all of them characterised by numerous specimens living in the neighbourhood of one another, we are brought to admit, that where the depth is more considerable, relatively large distances separate the places, where the animals of a certain species occur, from one another, or, that specimens of such a species are never numerous and not to be found at all at very many places. This is also proved by the circumstance, that the "Siboga" found again specimens of two species of *Scalpellum* only out of the ten which were collected by the "Challenger" in the Malay Archipelago. That the "Siboga" found again the only species of *Verruco* which the "Challenger" brought home from deeper water in that area, would not be in accordance herewith — in both cases, however, that species was also represented by very few specimens only. Finally, it seems astonishing in this connection that in several cases representatives of two and three species of the genus *Scolpellum*, sometimes moreover accompanied by a single specimen of a species of *Verruca*, were obtained with the same haul of the dredge, from the very same locality in consequence. Such stations seem to be very favourable for the occurrence of these animals: however, for these found there the same holds good, viz., that they were collected in very few specimens only¹⁾.

For some deepsea-species of *Scalpellum* it was possible to make out, that they produced only a few but relatively large eggs, and that their metamorphosis was an abbreviated one. There is good reason to suppose that these peculiarities are of importance for the question of their scarcity — we cannot say, however, that the one is explained by the other. Nevertheless, so far as our knowledge

¹⁾ It is obvious to admit, that the condition of the bottom in such cases is all-important. Without denying it, we must point out, however, that to judge from the information regarding the condition of the bottom as given in the list of the stations, its importance for the distribution of the *Cirripedia* is by no means so apparent as might be expected. So we can well say that many species of *Scalpellum* were found at places where the bottom was muddy, but several other species were obtained from a bottom of hard sand, of coarse sand or of coral sand etc. etc.

now goes, we must consider the deepsea-species of *Scalpellum* and *Verruca* as hermits; as the number of species of these genera especially is very large, most probably they furnish precious evidence for the ideas, about the influence of isolation on the origin of new species, which were brought forward originally by MORITZ WAGNER¹⁾ and were criticised and adopted in a much modified form only by WEISMANN²⁾.

For the geographical distribution of the Cirripeds the study of those collected by the "Siboga" has also been very instructive. With the exception of the pelagic forms, which are found attached to floating objects: pieces of wood, vessels, animals swimming at the surface: Cetaceans and others, etc. etc. and many of which are found in various parts of the world, these Crustaceans live attached to stones, shells of molluscs, corals etc.; the latter have good opportunity for active locomotion only in larval condition. But even in that condition, in consequence of their nearly microscopic size, their activity is only very limited; Nauplius- and Zoëa-larvae have limbs which enable them to move about, but more important is no doubt the distribution they are subjected to in a passive way, i. e. by means of the currents. However, even the latter distribution as a rule seems to be a very limited one: we only know very few non-pelagic Cirripeds which have a world-wide range or which occur in several of the eight provinces which were proposed by the present author in his Report on the "Challenger" Cirripeds for the animals of this group. The East-Indian or Malay Archipelago combined with the Philippines, Malacca, New-Guinea and the East coast of (British) India is one of these provinces; the investigation of the "Siboga"-material has shown again that this province indeed possesses its own Cirripeds, with the exception only of those species, which so to say spread themselves over its boundaries into other provinces, perhaps also of a few species which are at home in an adjacent province and came over its frontiers into the Malay Archipelago. Of the deepsea-Cirripeds we only know one single species, which can be said to occur at widely distant places of the earth's surface: *Scalpellum acutum*. The "Challenger" collected this species in the Atlantic Ocean (near the Azores) and in the Pacific (near the Kermadec-Islands) at a depth of 940-1800 m.; the "Talisman" also in the

1) WAGNER, MORITZ, Die Darwin'sche Theorie und das Migrationsgesetz der Organismen. Leipzig, 1868.

2) WEISMANN, AUGUST, Ueber den Einfluss der Isolirung auf die Artbildung. Leipzig, 1872.

Atlantic (not very far from the coast of Portugal) at a depth of 1925 m.; the "Siboga", finally, at three different places in the Malay Archipelago and at depths varying from 825 to 1265 m. But this does not change the rule, which still can be accepted as general, viz. that whereas several *genera* of *Cirripedia*, and those of the deepsea in the first place, are spread over the whole surface of the earth, the *species* of Cirripeds and especially the deepsea-species have been found to possess a very local distribution only.

To close this article a few words on the relation of the deepsea-forms to the extinct Cirripeds of which fossil remains have been preserved. The material collected with the "Siboga" in this regard also fully confirmed the conclusions arrived at by the working up of the material from the "Challenger". The species of the genus *Scalpellum*, which in the deepsea are so largely represented, have their representatives already in relatively old layers of the earth-crust, in secondary as well as in tertiary formations. We can even say, that a great majority of the species of the deepsea, with regard to an important anatomical characteristic (shape and structure of the so-called carina), show the greatest affinity to the oldest fossil forms (all those found in secondary formations); for this genus, therefore, we can safely admit that the deepsea-species, at least to a certain extent, show an archaic character. Side by side with the fossil *Scalpellum*'s, in the same formations and even in the same rocks or stones, numerous species of the genus *Pollicipes* were found. To this genus of which DARWIN alone enumerated 22 different fossil species belong the oldest known fossil Cirripeds and under the living it is still represented by half a dozen species. The "Challenger", however, did not succeed in collecting one single species of this genus even from slightly deeper water, which, when the author worked up the material of the "Challenger", gave rise to the remark, that the possibility of future investigations of the deepsea bringing to light species of the genus *Pollicipes*, could not be denied. Well then, the "Siboga" investigating the deepsea very carefully in one of the areas, where one of the living species of *Pollicipes* (*P. mitella*) is very generally distributed, did not obtain from deeper water one single specimen of a species of this genus either. So the exactness of the opinion pronounced in 1883, that, as far as the genus *Pollicipes* is concerned, the littoral or shallow water forms have preserved a more archaic character, has been completely confirmed by the results obtained with the "Siboga"-expedition. Of the genus *Verruca* a few species have also been found in older formations: one of these (*V. strömia*) is still

We suppose that the molecules are perfectly rigid and elastic and that they attract each other with forces acting at distances so great that we may consider the sphere of action as uniformly filled with matter.

For this case the value of Ψ is given by the equation

$$e^{-\frac{\Psi}{\theta}} = (2 \pi \theta m_1)^{\frac{3}{2} n_1} (2 \pi \theta m_2)^{\frac{3}{2} n_2} \int e^{-\frac{\epsilon_q}{\theta}} dx_{11} \dots dz_{2n_2} \dots \quad (2)$$

I shall represent the coordinates of the molecule k of the first kind by x_{1k} , y_{1k} and z_{1k} , and those of the molecule l of the second kind by x_{2l} , y_{2l} and z_{2l} .

The integration has to be extended to a $3(n_1 + n_2)$ -dimensional space, the notion of which is obtained if we take the $3(n_1 + n_2)$ coordinates of the centres of the molecules as cartesian coordinates of a single point, and give all possible positions to the molecules of the gas.

We must exclude from the space all those points at which a condition of one of the forms

$$\left. \begin{aligned} (x_{1k} - x_{1l})^2 + (y_{1k} - y_{1l})^2 + (z_{1k} - z_{1l})^2 < \sigma_1^2 \\ (x_{1k} - x_{2l})^2 + (y_{1k} - y_{2l})^2 + (z_{1k} - z_{2l})^2 < \sigma^2 \\ (x_{2k} - x_{2l})^2 + (y_{2k} - y_{2l})^2 + (z_{2k} - z_{2l})^2 < \sigma_2^2 \end{aligned} \right\} \dots \quad (3)$$

is fulfilled.

I have proved ¹⁾ in my dissertation that the large majority of the systems of a canonical ensemble may be considered as identical in all properties that are accessible to our means of observation. For all these equivalent or identical systems the value of the potential energy of the attractive forces is equal.

The sphere of action being uniformly filled, this quantity (ϵ_{q_0}) can be represented by

$$\epsilon_{q_0} = - \frac{\alpha_1 n_1^2 + 2 \alpha n_1 n_2 + \alpha_2 n_2^2}{2 V} \dots \dots \quad (4)$$

As to the potential energy of the repulsive forces, we need not speak of it when we take into account the conditions (3).

We shall obtain a good approximation, if, in the equation (2), we write ϵ_{q_0} instead of ϵ_q (which differs from ϵ_{q_0} only in a small part of the systems). By this, the exponential factor becomes a constant and we may put it before the sign of integration.

The quantity Ψ is thus expressed by the equation

¹⁾ l. c. p. 14

$$e^{-\frac{\Psi}{\theta}} = (2\pi\theta m_1)^{\frac{3}{2}n_1} (2\pi\theta m_2)^{\frac{3}{2}n_2} e^{-\frac{\epsilon_{q_0}}{\theta}} \int dx_{11} \dots dz_{2n_2} \dots \quad (5)$$

and its determination is reduced to the calculation of the integral on the right-hand side. Let the function $\chi(n_1, n_2)$ represent this integral.

In my dissertation I have determined this function to the degree of exactitude indicated above. Before proceeding to the determination of the terms of higher order I shall repeat the former calculation which now only wants further extension.

The $3(n_1 + n_2)$ -dimensional space of integration can be decomposed into $n_1 + n_2$ threedimensional spaces, each corresponding to one of the molecules. We shall divide these spaces into elements which are small in comparison with the volume of a molecule.

In order to determine the integral defining the function $\chi(n_1, n_2)$ we decompose it into a sum of products of $n_1 + n_2$ elements chosen in the spaces in question, each space being represented in the product by one and only one element.

In order clearly to see the way in which the products are formed with the restrictions imposed by (3), we proceed as follows: We number the spaces corresponding to the molecules of the first kind from 1 to n_1 , those corresponding to the molecules of the second kind from $n_1 + 1$ to $n_1 + n_2$, and we choose the elements in the order indicated by these numbers.

We have to consider that, if we have chosen for the centre of the k^{th} molecule ($k < n_1$) an element lying at a point x_{1k}, y_{1k}, z_{1k} , we must exclude from the $k + 1^{\text{th}}$ up to the n_1^{th} space those elements which are situated in spheres described with the radius σ_1 around the points of these spaces whose coordinates are equal to x_{1k}, y_{1k} and z_{1k} . Similarly we must exclude those elements from the spaces from $n_1 + 1$ up to $n_1 + n_2$, which lie within the spheres of radius σ described around the points of the spaces having for coordinates x_{1k}, y_{1k} and z_{1k} . If, further, in the space $n_1 + v_2$ an element has been chosen at a point with the coordinates $x_{2n_1+v_2}, y_{2n_1+v_2}, z_{2n_1+v_2}$ we must exclude in all following spaces the elements of spheres with radius σ_2 described around the points of those spaces having their coordinates equal to $x_{2n_1+v_2}, y_{2n_1+v_2}, z_{2n_1+v_2}$.

The elements in the spaces 1 to $n_1 + n_2 - 1$ having been chosen, there remains in the last space $n_1 + n_2$ a region $g_{n_1+n_2}$ for the choice of the $(n_1 + n_2)^{\text{th}}$ element.

In determining the sum we can first take together all those cases in which the elements of the spaces 1 to $n_1 + n_2 - 1$ are the same.

Considering that n_1 and n_2 are very great numbers, and that the

elements have been chosen quite arbitrarily, we easily see that the quantity $g_{n_1+n_2}$ must be the same for the greater majority of the possible ways of choosing the elements in the spaces up to the $(n_1 + n_2 - 1)^{\text{th}}$, and that we may therefore write

$$\chi(n_1, n_2) = g_{n_1+n_2} \chi(n_1, n_2 - 1) \dots \dots \dots (6)$$

$g_{n_1+n_2}$ being now a quite definite quantity, which it remains to determine.

It is very easy to find a first approximation to its value. For this purpose we have only to neglect the fact that the above mentioned spheres in the $(n_1 + n_2)^{\text{th}}$ space intersect. Doing so, we find

$$g_{n_1+n_2} = V - n_1 \frac{4}{3} \pi \sigma^3 - (n_2 - 1) \frac{4}{3} \pi \sigma_2^3 \dots \dots (7)$$

From (6) and (7) we deduce by successive reductions

$$\chi(n_1, n_2) = \chi(n_1) \prod_1^{n_2} \left(V - n_1 \frac{4}{3} \pi \sigma^3 - (v_2 - 1) \frac{4}{3} \pi \sigma_2^3 \right), \dots (8)$$

where we have affixed to the sign of the product the highest value that we have to give to the number denoted by the corresponding Greek letter. A similar notation will be used in later formulae.

It is easily seen that, with the degree of exactitude to which we have now confined ourselves, the value of $\chi(n_1)$ is given by

$$\chi(n_1) = \prod_1^{n_1} \left(V - v_1 \frac{4}{3} \pi \sigma_1^3 \right) \dots \dots \dots (9)$$

In order to push our approximation further, we have to determine $g_{n_1+n_2}$ more accurately. We must take into account that the spheres mentioned above intersect, and that we have therefore subtracted too much from the total volume.

Now three cases are to be distinguished.

1. Intersection between the spheres of radius σ described around the points corresponding to the centres of the molecules of the first kind. The distance x of the centres cannot be less than σ_1 and must be less than 2σ .

2. Intersection between the spheres of radius σ_2 described around the points corresponding to the molecules of the second kind. The distance of the centres must lie between σ_2 and $2\sigma_2$.

3. Intersection between the spheres of radius σ and σ_2 described around the points corresponding to the centres of molecules of the first and second kinds respectively. The distance x of the centres must lie between σ and $\sigma_2 + \sigma$.

I shall determine the parts corresponding to these three kinds of

intersections, which have been subtracted too much from V . These parts are equal for by far the majority of the possible combinations of elements in the spaces from the first up to the $(n_1 + n_2 - 1)^{\text{th}}$. We may suppose that the distribution of the points corresponding to the centres of molecules from 1 tot $n_1 + n_2 - 1$ is uniform in the $(n_1 + n_2)^{\text{th}}$ space.

1. The number of pairs of points (corresponding to molecules of the first kind) with mutual distance lying between x and $x + dx$ amounts to

$$2\pi n_1^2 \frac{x^2 dx}{V} \dots \dots \dots (10)$$

The common part of two spheres of radius σ having a central distance x is given by

$$\pi \left(\frac{4}{3} \sigma^3 - \sigma^2 x + \frac{x^3}{12} \right) \dots \dots \dots (11)$$

Hence, the total part subtracted too much on account of these intersections is equal to

$$\frac{2\pi^2 n_1^2}{V} \int_{\sigma_1}^{2\sigma_1} \left(\frac{4}{3} \sigma^3 x^2 - \sigma^2 x^3 + \frac{x^6}{12} \right) dx = \frac{\pi^2 n_1^2}{V} \left(\frac{8}{9} \sigma^6 - \frac{8}{9} \sigma^3 \sigma_1^3 + \frac{1}{2} \sigma^2 \sigma_1^4 - \frac{\sigma_1^6}{36} \right) (12)$$

2. The number of pairs of points (corresponding to the centres of molecules of the second kind) with a mutual distance between x and $x + dx$ is

$$2\pi (n_2 - 1)(n_2 - 2) \frac{x^2 dx}{V} \dots \dots \dots (13)$$

The common part of the spheres is found for this case, if in (11) we replace σ by σ_2 , so that we find for the part subtracted too much from V

$$2\pi^2 \frac{(n_2 - 1)(n_2 - 2)}{V} \int_{\sigma_2}^{2\sigma_2} \left(\frac{4}{3} \sigma_2^3 x^2 - \sigma_2^2 x^3 + \frac{x^6}{12} \right) dx = \frac{17(n_2 - 1)(n_2 - 2)}{16V} \left(\frac{2}{3} \pi \sigma_2^3 \right)^2 (14)$$

3. The number of pairs of points such that one point corresponds to the centre of a molecule of the first kind and one to that of a molecule of the second kind, the mutual distance lying between x and $x + dx$, amounts to

$$4\pi n_1 (n_2 - 1) \frac{x^2 dx}{V} \dots \dots \dots (15)$$

The common part of the spheres is now given by

$$\pi \left[\frac{2}{3} \sigma_2^3 + \frac{2}{3} \sigma^3 - \frac{\sigma_2^2 (x^2 + \sigma_2^2 - \sigma^2)}{2x} - \frac{\sigma^2 (x^2 + \sigma^2 - \sigma_2^2)}{2x} + \frac{(x^2 + \sigma_2^2 - \sigma^2)^2}{24x^3} + \frac{(x^2 + \sigma^2 - \sigma_2^2)^2}{24x^3} \right] \dots \quad (16)$$

and the total part subtracted too much from V by

$$4 \pi^2 \frac{n_1 (n_2 - 1)}{V} \int \left[\frac{2}{3} (\sigma^3 + \sigma_2^3) x^2 - \frac{1}{2} (\sigma^2 + \sigma_2^2) x^3 - \frac{1}{4} (\sigma^2 - \sigma_2^2)^2 x + \frac{1}{12} x^5 \right] dx = \pi^2 \frac{n_1 (n_2 - 1)}{V} \left(-\frac{1}{18} \sigma_2^6 + \sigma_2^4 \sigma^2 \right) \quad (17)$$

The value of $g_{n_1+n_2}$ is found by adding (12), (14) and (17) to (7) and substituting the obtained value in (8). By successive reductions we get

$$\chi(n_1, n_2) = \chi(n_1) \prod_1^{n_2} \left[V - n_1 \frac{4}{3} \pi \sigma^3 - (v_2 - 1) \frac{4}{3} \pi \sigma_2^3 + \frac{n_1^2}{V} \pi^2 \left(\frac{8}{9} \sigma^6 - \frac{8}{9} \sigma^3 \sigma_1^3 + \frac{1}{2} \sigma^2 \sigma_1^4 - \frac{1}{36} \sigma_1^6 \right) + \frac{17(v_2 - 1)(v_2 - 2)}{36} \frac{\pi^2 \sigma_2^6}{V} + \frac{n_1(v_2 - 1)}{V} \pi^2 \left(-\frac{1}{18} \sigma_2^6 + \sigma_2^4 \sigma^2 \right) \right] \quad (18)$$

It is easily seen that to the degree of approximation now required, $\chi(n_1)$ is represented by

$$\chi(n_1) = \prod_1^{n_1} \left(V - (v_1 - 1) \frac{4}{3} \pi \sigma_1^3 + \frac{17(v_1 - 1)(v_1 - 2)}{36} \frac{\pi^2 \sigma_1^6}{V} \right). \quad (19)$$

Substituting these values in (5), taking the logarithm of the result, and developing this logarithm in ascending powers of $\frac{1}{V}$, we find

$$\begin{aligned} -\frac{\Psi}{\theta} = & C + \frac{\alpha_1 n_1^2 + 2\alpha n_1 n_2 + \alpha_2 n_2^2}{2\theta V} + \\ & + \sum_1^{n_1} \left[\log V - \frac{v_1 - 1}{V} \frac{4}{3} \pi \sigma_1^3 - \frac{(v_1 - 1)(v_1 - 2)}{V^2} \frac{15}{36} \pi^2 \sigma_1^6 \right] + \\ & + \sum_1^{n_2} \left[\log V - \frac{n_1}{V} \frac{4}{3} \pi \sigma^3 - \frac{(v_2 - 1)}{V} \frac{4}{3} \pi \sigma_2^3 - \frac{(v_2 - 1)(v_2 - 2)}{V^2} \frac{15}{36} \pi^2 \sigma_2^6 - \right. \\ & \quad \left. - \frac{8n_1^2}{9V^2} \pi^2 \sigma_1^3 \sigma^3 + \frac{1}{2} \frac{n_1^2}{V^2} \pi \sigma^2 \sigma_1^4 - \frac{1}{36} \frac{n_1^2}{V^2} \pi^2 \sigma_1^6 - \right. \\ & \quad \left. - \frac{16n_1(v_2 - 1)}{9V^2} \pi^2 \sigma_2^3 \sigma^3 + \frac{n_1(v_2 - 1)}{V^2} \pi^2 \sigma_2^4 \sigma^2 - \frac{1}{18} \frac{n_1(v_2 - 1)}{V^2} \pi^2 \sigma_2^6 \right] \quad (20) \end{aligned}$$

C being the part which is independent of V .

Since n_1 and n_2 are very large numbers, we easily see that the expression (20) can be transformed to

$$\begin{aligned}
 -\frac{\Psi}{\theta} = C + \frac{\alpha_1 n_1^2 + 2\alpha n_1 n_2 + \alpha_2 n_2^2}{2\theta V} + (n_1 + n_2) \log V - n_1^2 \frac{\beta_1}{V} - \frac{5}{16} n_1^3 \frac{\beta_1^2}{V^2} \\
 - n_2^2 \frac{\beta_2}{V} - \frac{5}{16} n_2^3 \frac{\beta_2^2}{V^2} \\
 - 2n_1 n_2 \frac{\beta}{V} \\
 - \frac{8 n_1^2 n_2}{9 V^2} \pi^2 \sigma_1^3 \sigma^3 + \frac{1 n_1^2 n_2}{2 V^2} \pi^2 \sigma_1^4 \sigma^2 - \frac{1 n_1^2 n_2}{36 V^2} \pi^2 \sigma_1^6 \\
 - \frac{8 n_1 n_2^2}{9 V^2} \pi^2 \sigma_2^3 \sigma^3 + \frac{1 n_1 n_2^2}{2 V^2} \pi^2 \sigma_2^4 \sigma^2 - \frac{1 n_1 n_2^2}{36 V^2} \pi^2 \sigma_2^6 \dots (21)
 \end{aligned}$$

where β_1 has been put for $\frac{2}{3} \pi \sigma_1^3$, β_2 for $\frac{2}{3} \pi \sigma_2^3$ and β for $\frac{2}{3} \pi \sigma^3$.

Finally, differentiating Ψ with respect to V , we find the following equation for the pressure

$$\begin{aligned}
 \frac{p}{\theta} = \frac{n_1 + n_2}{V} + \frac{n_1^2 \beta_1}{V^2} + \frac{5 n_1^3 \beta_1^2}{8 V^3} + \frac{n_2^2 \beta_2}{V^2} + \frac{5 n_2^3 \beta_2^2}{8 V^3} + \frac{2 n_1 n_2 \beta}{V^2} \\
 - \frac{n_1^2 n_2}{V^3} \beta_1^2 \left(-4 \frac{\beta}{\beta_1} + \frac{9}{4} \frac{\beta}{\beta_1} \frac{\sigma}{\sigma_1} - \frac{1}{8} \right) \\
 - \frac{n_1 n_2^2}{V^3} \beta_2^2 \left(-4 \frac{\beta}{\beta_2} + \frac{9}{4} \frac{\beta}{\beta_2} \frac{\sigma}{\sigma_2} - \frac{1}{8} \right) \\
 - \frac{\alpha_1 n_1^2 + 2\alpha n_1 n_2 + \alpha_2 n_2^2}{2\theta V^2}.
 \end{aligned}$$

The quantity θ is proportional to the absolute temperature.

The expression for p is of course symmetrical in the quantities relating to the two kinds of molecules, and it would have been possible to find the same result by arranging the spaces in a different order. Our result agrees with that of HAPPEL, the only difference being in the notations.

Botany. — "*Lindeniopsis*. A new subgenus of the *Rubiaceae*". By Dr. TH. VALETON (Buitenzorg).

During an official journey through the island of Billiton in March 1907 Mr. HAM, Inspector of Forests in the Dutch East Indies, gathered a small, but not unimportant herbarium collection, which he gave over to me for study.

The importance of this collection mainly depends on the fact, that it was formed on lands, which are extremely rare in the Indian Archipelago, and are as yet florally almost unknown. These are the so-called "*padang*" lands (compare VERBEEK in *Jaarboek Mijnwezen* 1897, p. 60 and 61). The soil of these lands consists of young, loose sediments of recent origin, namely quartz sand and clay, both often containing iron and manganese; the soil, however, owes its peculiar character to the presence of a mineral, which the Chinese call *fo sau kak* and which consists of quartz sand, which has been moulded together by organic acids into a pretty firm, dark brown sand-stone.

"These *padang* lands are characterized by a sparse and peculiar vegetation, in consequence of the small permeability to water of the "*fo sau kak*", so that level *padang*-lands are frequently inundated after heavy rains, and the roots of the plants, which can only penetrate with difficulty into the hard "*fo sau kak*", rot and die off." (VERBEEK l.c.).

Besides in Billiton, these *padang* soils are also found in Banka between Doeren and Boekit (VERBEEK l.c.). In other parts of the Archipelago they do not appear to be known. The most important of these lands are found in the north and north-east of the island, between Boeding and Manggar, and were studied botanically by Mr. HAM.

From verbal information and from the journal of the voyage, which Mr. HAM kindly lent me for perusal, I obtained the following data:

The appearance of the *padang* soils is not everywhere the same. Mr. HAM distinguishes: 1 *grass padang*, often rich in flint, where grasses and sedge-grasses predominate, 2 *fern padang* where ferns (*Pteris aquilina* L., *Nephrolepis acuta* PRESL.), form almost the whole vegetation, being only mixed with *Xyris microcephala* HASSK., *Fimbristylis* spec., *Melastoma* spec., *Calophyllum pulcherrimum* WALL., *Psychotria viridiflora* BL. and 3 *sand padang*, where the soil consists of blinding white quartz sand. The white layer varies in thickness from $\frac{1}{2}$ —5 centimetres; under this the soil is grey, obviously through humus, and sometimes it is grey immediately below the

surface, when fine, black humus or mosses occur at the bottom. The vegetation nowhere forms a compact mass or sod. Groups of low and high shrubs, generally with higher shrubs or small trees in the middle, alternate with a lower vegetation, which is also always limited to separate spots or clumps, so that the white sand can everywhere be seen through it, and in many places even has the upper hand. Of the plants which were collected here, the following are mentioned as characteristic:

Drosera Burmanni VAHL. in the dampest parts, forming dark-red areas, when seen from a distance, often placed on small columns of sand; *Fimbristylis* spec., *Rhynchospora* spec., *Xyris microcephala* HASSK. and *Xyris bancana* MIQ.; more rarely *Salomonina oblongifolia* D.C., *Lindernia stemodioides* MIQ., *Thuarea sarmentosa* PERS.

Of the shrubs the following are prominent: *Baeckea frutescens* L., which in low-lying padangs forms more than half of the vegetation, and reminds one very much of the *Calluna* of European heaths, *Jambosa buxifolia* MIQ., *Leptospermum glavescens* SM., *Leucopogon malayanus* JACK., *Vaccinium malaccense* WIGHT, *Cratoxylon glaucum* KORTH., *Calophyllum pulcherrimum* WALL., *Timonius* spec., *Garcinia bancana* MIQ., *Syzygium variifolium* MIQ., the last three arborescent.

On the lowest lying padangs south of Manggar and near Boeding, where *Baeckea frutescens* and *Fimbristylis* spec. formed the chief vegetation, *Ischaemum* spec., *Archytaea VahlII* CHOISY, *Wormia suffruticosa* GRIFF., *Melaleuca minor* SM. and a non-determinable species of *Eugenia* were also noticed; in addition mosses and lichens. Further there were collected in these localities *Rhodomyrtus tomentosa* WIGHT, *Nepenthes* spec., *Tristamia obovata* R. BR., *Dischidia* spec. *Bromheadia palustris* LINDL. [Orchidea], *Isachne australis* R. BR. *Burmanna bancana* MIQ., a species of *Lucinaea*, which is probably new, and finally a new Rubiaceae, about which I wish to make a communication here.

The above-described formation has in consequence of the predominant occurrence of the *Calluna*-like *Baeckea frutescens* a superficial resemblance to the sandy and boggy heaths of Northern Europe. Already JUNGHUHN, in his description of the Battak countries I, p. 158, refers to an *Erica*, which above the forest zone characterizes the alpine flora in company of other woody Myrtaceae, and he doubtless means *Baeckea frutescens*. From Southern China and the Philippines to New-Guinea, where BECCARI found the plant at Goldfinck Bay (altitude?) and WICHMANN on the G. Siöp at about 800 Meters, the area of distribution of this species extends; it is wanting in Java and its nearest allies (numerous *Baeckea*-species) inhabit Australia.

Everywhere it is characteristic of physiologically dry plateaus and rarely descends to the low-lying plains, as in the present case. *Drosera* and the *Cyperaceae* also tend to emphasize the resemblance to heaths.

Through the other vegetation, of which the sclerophyllous and sclerocarpous Myrtaceae form an important constituent, this formation, however, approximates much more to that which was called by SCHIMPER (Pflanzengeogr. p. 538) "*Hartlaubformation*" and of which he describes a number of regions, occurring round the Mediterranean, in California, in Chili, in South-Africa and in South-Australia. These regions are all characterized by dry and hot summers, alternating with moist winters. Hence climatologically there is little resemblance between these and the padang-formation of Banka and Biliton, where it rains almost the whole year. As regards the condition of the soil, there is, on the other hand, a resemblance with the South-Australian "*scrublands*", described by SCHOMBURGK in his Flora of South-Australia 1875. (See SCHIMPER l. c. p. 559).

The dominant influence of the soil on the character of the formation cannot here be doubted; this influence, which according to SCHIMPER is relatively rare in the Tropics, has been but little investigated. (See SCHIMPER l. c. p. 405. Edaphische Wirkungen in den Tropen).

The padang-formation does not correspond even roughly with any of the vegetation-pictures and formations, mentioned in that chapter. As has been mentioned, it can only, to some extent, be compared with tropical alpine floras and with the "*Hartlaubformation*".

The plants, collected by Mr. HAM, probably do not represent a complete, but nevertheless give a very typical picture of this rather poor flora. As regards the distribution of these plants, it is at once noticeable, that not a single one of these occurs in Java, with the exception of two wide-spread grasses, which have crept in from the beach, namely *Thuarea sarmentosa* and *Isachne australis*, and with the exception of the two pantropic ferns and of *Psychotria viridiflora*, which plants were, moreover, not found in the typical sand padang. A wide distribution from Malacca to Australia through the northern part of the Archipelago, but excluding Java (probably up to and including Timor), is observed in the case of *Baeckea frutescens*, and also of *Leptospermum flavescens*, *Rhodomyrtus tomentosa*, *Melaleuca minor*, *Drosera Burmanni*, *Salomonina oblongifolia* and *Bromheadia palustris*. From Malacca and Borneo are known: *Calophyllum pulcherrimum*, *Garcinia bancana*, *Vaccinium malaccense*, *Leucopogon malayanus*, *Archytaea Vahlü*, *Wormia suffruticosa*. From Banka

and Billiton only the following are known: *Jambosa buxifolia*, *Syzygium variifolium*, *Tristania obovata*, *Schima bancana*, *Xyris bancana* and *Lindernia* (*Vandellia*) *stemodioides*; *Cratoxylum glaucum* and a *Lucinaea* spec. nova were only known from Borneo. The as yet undetermined *Eugenia*, *Nepenthes*, *Dischidia* and *Ischaemum*, and a few others, are doubtful in this respect.

Endemic, as far as our present knowledge extends, is only the new species, now to be described. Unfortunately data are wanting about the dimensions and habit of this plant, but it belongs to the suffruticose inhabitants of the low sand-padangs, referred to above; it is among the species, poor in individuals, and it reaches a height of $\frac{3}{4}$ —2 metres. The rod-like erect branches which are often 60 centimetres long, and bear at their tops the crowded inflorescences with grey hairs, the small stiff, aciculate, erect leaves, all these characters indicate a strongly xerophytic nature.

At the first examination this species seemed to me to constitute a completely new genus. It belongs to the tribe *Cinchoneae* of the sub-order *Cinchonoideae* (K. SCHUMANN), and to the sub-tribe *Hillieae*. On applying the analytical key, prepared by K. SCHUMANN (Natürl. Pflanz. Fam. IV 4 p. 42) one does not arrive at any genus in particular, but in the immediate neighbourhood either of *Cosmibuena* RUIZ and PAVON, or of *Coptosapelta* KORTH., according as to whether one takes the style to be little or very much longer than the corolla-tube. A closer comparison with the genus *Cosmibuena*, to which a small number of Central- and South-American, epiphytic shrubs belong, at once, however, reveals considerable differences in the structure of the calyx, stamens, stigma and in the dehiscence of the fruit, so that there can be no question of a union with this genus, although in habit and in the shape of the flowers the agreement is closer than with *Coptosapelta*. As regards the latter genus, it is said in the above-mentioned key: "style quadrangular and hairy", so that, if one were to adhere strictly to this, one would be forced to set up a new genus for our species, in which the style is cylindrical and glabrous. On further comparison with the characters given in the generic diagnosis for *Coptosapelta*, the following differences are also found: Calyx, small, saucer-shaped, five-toothed in *Coptosapelta*; in the new species much longer than the calyx-tube, divided to its base into five lanceolate, pointed, erect divisions. — Corolla-tube very short, as long as or shorter than the lobes of the limb, and hairy at the tube-mouth, in *Coptosapelta*; in the new species 4—6 centimetres long, thin and straight, much longer than the lobes of the limb, and glabrous at its mouth. — Anthers almost as

long as the lobes of the limb and hirsute on their dorsal side, with deeply cleft base, in *Coptosapelta*; here much longer than the lobes of the limb, glabrous, and with a two-lobed base. Seeds with a regularly fringed wing in *Coptosapelta*; here surrounded by an entire wing. Finally as regards the habit, the two known species of *Coptosapelta* are high-climbing shrubs with fairly large leaves and many-flowered pendulous panicles of small flowers, whereas the new species is a small erect shrub with erect cymes of few, prominent flowers.

Superficially there seems therefore abundant reason for setting up a new genus for this new species, and on account of the great resemblance in habit, leaves, inflorescence, calyx and corolla, to the American genus *Lindenia*, which belongs to the tribe of the *Rondeletieae*, I gave it the name *Lindeniopsis*.

A closer comparison with *Coptosapelta flavescens* KORTH, which occurs in Java, induced me, however, to withdraw this genus and to bring the new species under *Coptosapelta*. Some of the points of difference, deduced from the literature, proved to be the result of errors in the existing descriptions. For instance, the style in *C. flavescens* is not *quadrangular* and *hairy* as described by SCHUMANN, but, except at the top, cylindrical and glabrous, as in the new species; the calyx is not saucer-shaped, but deeply divided into five divisions, and resembles, except in size, that of the new species, and the mouth of the tube is not hairy, but quite glabrous. In this way a number of the enumerated points of difference already disappear.

There is further perfect similarity in the structure of the ovary and fruit of the two plants. The very peculiar stigma, which in contradistinction to the neighbouring genera, is not two-lobed, but quite entire, and receives pollen on the stigmatic papillae which cover the whole of its hairy surface. The anthers are identical in structure and in their mode of attachment. Finally, what is very important, the pollen of the new species has, like that of *C. flavescens*, an exine with net-shaped thickenings of wide mesh, and, as would appear from the figures in the *Flora brasiliensis*, the plant herein differs completely from the other genera of the *Hillieae*. Having regard to all these similarities, there can be no doubt, that our new species must be included in the genus *Coptosapelta*, but forms in it a special, monotypic sub-genus.

As a morphological peculiarity, which confirms the relationship to *C. flavescens*, I here draw attention to the glands, which alternate with the calyx divisions, and have, as far as I know, not yet been

described in any other of the *Rubiaceae* (with the possible exception of *Dichilanthe* Hook.).

They have the same structure as the colleters, resembling intestinal glands, which in this genus, as in most *Rubiaceae*, are placed at the inside of the base of the stipules¹⁾ and are also found on the leaf base in *Apocynaceae* and in *Loganiaceae*. They are found in the new species, as in *C. flavescens*, alternating with the calyx divisions singly or two together; in the latter species they are however, only $\frac{1}{5}$ mm. long and have hitherto been overlooked by investigators; in the new species they are well over 1 to 1.5 m.m. in length.

Perhaps, on closer examination, they will also be found to exist in other *Rubiaceae*. Obviously they must be interpreted as rudimentary stipules of the sepals.

Coptosapelta KORTH. Descriptio nova: Calycis tubus ellipsoideus, limbus eo nunc brevior nunc duplo longior, persistens, dentatus vel ad basin usque 5-partitus, segmentis erectis imbricatis cum glandulis parvis stipularibus erectis teretibus singulis vel binis alternantibus. Corolla coriacea tomentosa, hypocraterimorpha, tubo brevi vel longo, gracili, tereti, intus glabro vel fauce hirta, limbi lobi obovato-lineares aestivatione contorti. Stamina 5 ori corollae inserta, filamentis brevibus subulatis; antherae oblongae vel lineares apice apiculatae, basi subbilobae vel bipartitae glabrae vel dorso hirsutissimae, dorso prope basin affixae, patentes demum saepe tortae. Pollinis granula subglobosa, poris 3², insigniter reticulata. Discus carnosus cupularis. Ovarium biloculare. Stylus teres glaber elongatus corollae tubum aequans apice exsertus. Stigma magnum integrum, fusiforme vel clavatum, in alabastro per longitudinem striatum, puberulum; ovula in loculis numerosa, placentis magnis septo affixis peltatis linearibus apice et basi liberis dense imbricatim affixa, peltata, marginata, ascendencia. Capsula obovoidea lateraliter compressa obsolete costata calyce longius persistente coronata, glabrescens ad medium versus loculicide bivalvis, vel demum saepe quadrivalvis. Semina placentae cylindricae, subcarnosae, loculum implenti extus affixa, peltata, imbricata, erecta, testa membranacea in alam hyalinam nunc insigniter fimbriatam nunc subintegram crenulatam radiatum striulatam expansa, albumine carnosio; embryo rectus parvus radícula tereti infera.

Frutices nunc alte scandentes nunc parvi erecti, canescenti-sericeo-villosi, ramulis tetragonis foliis coriaceis, subtus \pm villosulis. Stipulae interpetiolares parvae ovato-trigonae.

¹⁾ Vide SOLEREDER, Anat. Charakt. der *Rubiaceae* 1893, p, 179.

Cymae terminales et in axillis superioribus trichotomae nunc densiflorae et ample paniculatae pendentes, nunc pauciflorae erectae. Flores brevissime pedicellati, bracteolis (prophyllis) 2, pedicello insertis calyce appressis eoque brevioribus instructi, nunc parvi nunc conspicui.

Subgenus I *Eucoptosapelta* VAL. Calycis limbus ovario brevior. Corollae tubus brevis, limbi lobos aequans vel illo brevior, faucis orificium glabrum vel hirsutum. Antherae lineares, basi bifidae, dorso dense villosae, demum tortae. Stigma elongato-fusiforme vel quadrangulare. Seminum ala fimbriata. Frutices alte scandentes ramulis subteretibus. Foliis majusculis patentibus subtus ad nervos villosis. Paniculae terminales foliatae multiflorae, densiflorae, pendentes.

1. *C. flavescens* KORTH., (*Stylocoryne racemosa* haud CAVANILLES, MIQ.; *St. tomentosa* BL.): Corollae tubus limbi lobos circiter aequans, faux glabra. Calycis tubus brevis.

Habitat: Malaccâ, Burma, Borneo, Java.

2. *C. Griffithii* Hook.: Corollae tubus limbi lobis multo brevior. Faux dense hirsuta. Calycis tubus elongatus.

Habitat: Malacca, Singapore.

Subgenus II: *Lindeniopsis* VAL. Calycis limbus ovario plus duplo longior, ad basin usque partitus segmentis erectis lanceolatis acutis. Corollae tubus gracilis lobos pluries superans, faucis orificio glabro. Antherae oblongae basi bilobae, glabrae. Stigma magnum, clavatum. Seminum ala subintegra.

Frutices parvi erecti, ramulis acute tetragonis erectis elongatis, foliis parvis erectis rigide-coriaceis, spinuloso-apiculatis subtus appresse villosis. Cymae terminales et in axillis superioribus trichotomae, pauciflorae, erectae.

3. *C. Hammii* VAL. Characteres subgeneris.

Habitat: Biliton.

Botany. — “*Contribution N^o. 1 to the knowledge of the Flora of Java.*” (Third Continuation)¹). By Dr. S. H. KOORDERS.

§ 6. Further data concerning *Oreiostrongylus Pullei* Gamble.

§§ 1. Additions and corrections to p. 674—686 of the “Proceedings”.

The proof-corrections, which Mr. GAMBLE sent me from England last April, were, nevertheless, much to my regret, received by the printers too late for incorporation in the number of the Proceedings

¹) Continued from p. 773 of the Proceedings of the Royal Academy of Sciences, Amsterdam, ordinary meeting of the Math. and phys. section April 9th 1908.

of the Royal Academy of Sciences, which appeared in April 24th 1908. I now append these proof-corrections, which date from last April and are due to Mr. J. S. GAMBLE, to whom I tender my thanks:
p. 683 line 11 from bottom: *after* Kurz, *insert*: Munro in Trans. Linn. Soc. London. XXVI. 146.

p. 683 line 4 from bottom: *before* (GAMBLE msc.) *insert*: and possibly so establishing a connection between it and the *Schizostachyum*, the description of which by HASSKARL and KURZ are somewhat imperfect”.

p. 683 line 4 from bottom: *after* additional *insert*: material.

p. 684 line 16 from bottom: *before* conspecific *insert*: very probably.

§§ 2. On the fruits of *Oreiosiachys* GAMBLE, which have been discovered by Mr. K. A. R. BOSSCHA.

On p. 684 of the English edition of the Proceedings of the Royal Academy of Sciences, Amsterdam, meeting of February 28th 1908, it was pointed out by me, that it might be possible to trace this species locally by means of the constant native name, i. a. in order to obtain the fruits, as yet unknown.

I am now privileged to announce the collection of these fruits, as yet unrecorded in the literature, and to communicate certain further details, taken from a letter of Dr. TH. VALETON, dated Buitenzorg May 12th 1908 and from the enclosures to his letter, for which I here wish to thank him.

“Enclosed I am sending you three fruits of *Oreiosiachys* GAMBLE, of which ten were sent me in November 1903 by Mr. K. A. R. BOSSCHA, after I had received in May flowers from the same station. I propose that you should send these to Mr. GAMBLE, in order that he may complete his generic description, which has been published by you. I am also sending you some notes about observations, made in the locality by Mr. BOSSCHA, and further some references to the literature, which already exists about this species.” (Dr. VALETON msc. May 12th 1908).

I quote below the paragraphs in the letter referring to the observations of Mr. BOSSCHA.

“Mr. BOSSCHA drew my attention to the fact, that the plant bears flowers in two ways, namely at the end of small branches¹⁾ with

¹⁾ Mr. GAMBLE and I have not, as yet, had at our disposal these thick-leaved branches, flowering at their ends, but only the sterile leafy branches of JUNGHUHN and the almost leafless flowering twigs, without fruits, of PULLE described by Mr. GAMBLE.

thick foliage and also close to the stem on quite leafless lateral branches."

"Mr. BOSSCHA also told me, that when he arrived in Malabar in 1896, old natives, who were thoroughly familiar with the forests of the district in which the plant occurs, were ignorant of the fact, that this bamboo had ever flowered. In 1902 the flowering began, and it recurred fairly regularly until 1906. Since then the species has died off in most places, and is now decidedly scarce. This year it has again, however, been found in flower in Taloen (a plantation on the Malabar) in May 1908."

"Now, however, young plants are beginning to appear every where, obviously self-sown."

"This phenomenon partly agrees therefore with what has been observed in the case of other bamboo-species in British India, although the flowering period has been especially long in this case". (Dr. VALETON msc. May 12th 1908).

While I here refer with special appreciation to the fact that Dr. TH. VALETON placed the three fruits and the above-mentioned data at my disposal, I need scarcely say, that I at once complied with his request, and sent the fruits, received by me on June 17th to Mr. GAMBLE. Although the examination of the fruits is not yet complete, and will be referred to later, as soon as the supplementary diagnosis by Mr. GAMBLE shall have been received, I nevertheless consider the discovery, by Mr. K. A. R. BOSSCHA, of the fruits of this bamboo-species of sufficient importance to call for attention here. It is evident from Dr. VALETON's letter quoted above that the receipt by him at Buitenzorg from Mr. BOSSCHA of the fruits of *Oreiostachys* GAMBLE with the flowers (the fruits having remained unknown in the literature until now) was prior to Mr. GAMBLE's discovery of the type of a new genus in the flowers collected by Dr. PULLE.

It may further be mentioned, that the fruits discovered by Mr. BOSSCHA, and the flowers collected by Dr. PULLE on the Wajang-Windoe in 1906, are from the same district, namely the locality mentioned on p. 686 of these Proceedings.

In an enclosure to his letter to me of May 12th Dr. VALETON gives certain specific names, which he regards as synonyms (*Bambusa elegantissima* Hassk., etc.) and also the other literature references relating to this subject. Since these names, and the literature references, with the exception of "MUNRO" (see above, §§ 1), have already been published by Mr. GAMBLE and myself in the Proceedings of April 24th, it seems to me unnecessary to repeat them.

Although I have not had at my disposal the terminally flowering

branches with thick foliage collected by Mr. K. A. R. BOSSCHA, on which Dr. VALETON's addition to GAMBLE's diagnosis is based, I can now conform this amplification of GAMBLE's diagnosis, sent me on May 12th by Dr. VALETON, thanks to supplementary material received to-day (June 27th 1908) from Dr. A. PULLE (Utrecht) and at once forwarded to Mr. GAMBLE. In order to complete the diagnosis of *Oreiostachys*, and to settle the question of the further probable synonymy of this interesting species, a question raised by Mr. GAMBLE and myself in the Proceedings of April 24th there now only remain as desiderata the collection of stem-sheaths and the examination of the authentic specimens of *Bambusa elegantissima* HASSK. and *Schizostachyum elegantissimum* (HASSK.) KURZ, which so far have not been found, either by Dr. VALETON at Buitenzorg, or by myself at Leiden or Utrecht.

Leiden, June 27th 1908.

Physics. — “*On the law of molecular attraction for electrical double points*”. By Prof. J. D. VAN DER WAALS Jr. (Communicated by Prof. Dr. J. D. VAN DER WAALS).

Several physicists have already urged the supposition that the molecular attraction results from the electric forces exercised by electrically charged particles which are contained in the molecule. One of the simplest suppositions we can make in trying to explain the molecular action from an electrical origin is that the molecules will behave as electrical double points. This has, in fact, been assumed by Mr. REINGANUM¹⁾ and by Mr. SUTHERLAND²⁾.

As the formula for the action between two electrical double points, which is the same as that for the action between two magnetic molecules³⁾, contains $\frac{1}{r^4}$ as a factor, — r representing the distance between the two double points, — these physicists concluded that the molecules would attract one another with a force proportional to $\frac{1}{r^4}$. The opinion that the electron-theory supports the supposition of a molecular attraction proportional to $\frac{1}{r^4}$ has accordingly been often advanced.

¹⁾ M. REINGANUM, Phys. Zeitschr. 2, 241 (1901); DRUDES Ann. 10, 334 (1903).

²⁾ W. SUTHERLAND, Phil. mag. (6) 4, 625 (1902).

³⁾ Cf. J. C. MAXWELL, A treatise on electr. and magn. Art. 387.

On closer inspection, however, this opinion proves to be unfounded. If the double points have not yet yielded to the directing couples which they exercise on one another, and if therefore the axes may be directed in any direction, the mutual action will as often be a repulsion as an attraction, i. e. the mean attraction will be zero. If on the other hand we might assume that they had perfectly yielded to the directing couples, they would attract each other with forces proportional to $\frac{1}{r^4}$. It is, however, evident that the molecules will only partially have yielded to the couples, and that they will be more perfectly directed according as they have approached each other more closely and therefore lie in a stronger field of forces. The consequence will be that the resulting molecular action will be an attraction which with increasing r varies more rapidly than $\frac{1}{r^4}$. This circumstance has not escaped the attention of REINGANUM and of SUTHERLAND. They, however, thought that the law of attraction would only slightly deviate from $\frac{1}{r^4}$ and assumed this law to be, at least approximately, accurate.

In 1900 the present writer expressed the supposition that the resulting attracting forces would vary more rapidly than $\frac{1}{r^7}$). It is true that he founded his calculation on a somewhat different supposition as to the nature of the molecules, namely that they would act not as constant but as periodical double points, but this difference is probably not essential, as the law of attraction for vibrating double points will not improbably agree in a high degree with the law for constant double points, at least when the mutual distance of the molecules is small compared with the wave-length, which condition is satisfied in the case of gas-molecules at pressures of the order of one atmosphere.

At present it is my intention to investigate more accurately what will be the law of the resulting attraction for constant double points. We shall see that the attraction in this case really varies more rapidly than proportional to $\frac{1}{r^7}$. To render a rigorous treatment of this problem possible, we shall assume the following condition to be satisfied :

¹⁾ J. D. VAN DER WAALS Jr., Dissertation, Amsterdam, p. 85.

1st. The molecules are electrical double points with a constant moment m .

2nd. The mean distance of the molecule is so great that we may neglect the cases in which more than two molecules interact.

3rd. The velocities and the accelerations of the molecules have a value relatively so small, that we may assume that their field of force does not differ appreciably from the electrostatic field of the double points. A consequence of this supposition is that the energy of the system may be represented by :

$$L - \frac{1}{2} \sum m \mathcal{E} \cos \varphi + C$$

where L represents the kinetic energy of the system, \mathcal{E} the electric force, φ the angle between the axis of a molecule and the electric force at that place, and C a constant which does not depend on the velocity and the mutual position of the molecules.

If this last condition is satisfied the statistical mechanical considerations of BOLTZMANN and of GIBBS are directly applicable to our problem. If on the other hand it is not satisfied these considerations cease to be applicable and then it is impossible to solve the problem before a statistical treatment of a continuum as the electromagnetic field has been worked out, which is analogous to GIBBS's treatment of systems with a finite number of degrees of freedom ; this however is not the case as yet. A rigorous discussion of the case that the molecules are vibrators is therefore as yet impossible and so we shall have to confine ourselves to the supposition of constant double points.

Let us imagine a molecule A and at a distance r another molecule B . The angle between the axis of A and the radius vector will be called ϑ , then the electric force exerted by A at the point where the molecule B is found, will be :

$$\mathcal{E} = \frac{m}{3r^3} \sqrt{4 \cos^2 \vartheta + \sin^2 \vartheta} = \frac{m}{3r^3} \sqrt{3 \cos^2 \vartheta + 1}.$$

If again φ is the angle between \mathcal{E} and the axis of B then the potential energy of B is:

$$- \frac{m^2}{3r^3} \sqrt{3 \cos^2 \vartheta + 1} \cdot \cos \varphi$$

According to the well-known theory of BOLTZMANN and GIBBS the probability that the angle φ will fall between the limits φ and $\varphi + d\varphi$ and the angle ϑ between the limits ϑ and $\vartheta + d\vartheta$ is:

$$\frac{1}{4} \sin \varphi d\varphi \cdot \frac{\sin \vartheta d\vartheta \cdot e^{-\frac{m^2 \sqrt{3 \cos^2 \vartheta + 1} \cdot \cos \varphi}{3r^3 t}}}{\int \int e^{-\frac{m^2 \sqrt{3 \cos^2 \vartheta + 1} \cdot \cos \varphi}{3r^3 t}} d\varphi d\vartheta}$$

where t represents twice the mean kinetic energy for one degree of freedom or $\frac{2}{3}$ of the mean kinetic energy of the motion of the centre of gravity of a molecule. So we find for the mean value of the potential energy of a molecule at a distance r from another molecule:

$$E = - \int_0^\pi \int_0^\pi \frac{m^2}{3 r^3} \sqrt{3 \cos^2 \vartheta + 1} \cos \varphi \cdot e^{-\frac{m^2 \sqrt{3 \cos^2 \vartheta + 1} \cdot \cos \varphi}{3 r^3 t}} \frac{1}{4} \sin \varphi d\varphi \cdot \sin \vartheta d\vartheta.$$

or ¹⁾

$$E = + \frac{t}{4} \int_0^\pi \sin \vartheta d\vartheta \int_0^\pi \cos \varphi \cdot e^{-\frac{m^2 \sqrt{3 \cos^2 \vartheta + 1} \cdot \cos \varphi}{3 r^3 t}}$$

Let us put $\frac{m^2}{3 r^3 t} = c$ and $\sqrt{3 \cos^2 \vartheta + 1} = x$, then we find by partial integration :

$$E = - \frac{t}{4} \int_0^\pi \sin \vartheta d\vartheta \left\{ e^{cx} + e^{-cx} - \frac{1}{cx} (e^{cx} - e^{-cx}) \right\}$$

If we take into account that :

$$\int_0^\pi f(\vartheta) d\vartheta = \int_0^{\frac{\pi}{2}} \{f(\vartheta) + f(\pi - \vartheta)\} d\vartheta,$$

then we see that instead of taking the above integral between the limits 0 and π we may take twice this integral between 0 and $\frac{\pi}{2}$.

Now we may introduce x as new variable, writing :

$$\cos \vartheta = \frac{1}{\sqrt{3}} \sqrt{x^2 - 1}, \text{ and therefore } - \sin \vartheta d\vartheta = \frac{1}{\sqrt{3}} \frac{x dx}{\sqrt{x^2 - 1}},$$

making use of the following series :

$$e^{cx} + e^{-cx} - \frac{1}{cx} (e^{cx} - e^{-cx}) = 4 \left\{ \frac{c^2 x^2}{3!} + \frac{2c^4 x^4}{5!} + \frac{3c^6 x^6}{7!} + \dots \right\}$$

we find :

$$\begin{aligned} E &= - \frac{2t}{\sqrt{3}} \int_1^2 \frac{x dx}{\sqrt{x^2 - 1}} \left\{ \frac{c^2 x^2}{3!} + \frac{2c^4 x^4}{5!} + \frac{3c^6 x^6}{7!} + \dots \right\} \\ &= - \frac{t}{\sqrt{3}} \int_1^4 \frac{dy}{\sqrt{y - 1}} \left\{ \frac{c^2 y}{3!} + \frac{2c^4 y^2}{5!} + \frac{3c^6 y^3}{7!} + \dots \right\} \end{aligned}$$

¹⁾ I am indebted for the reduction of this integral to Prof. Dr. W. КАРПЕУН from Utrecht, to whom I gladly express my thanks for his kind assistance.

If again we substitute $\sqrt{y-1} = z$ then the different terms assume the following form :

$$\int_1^4 \frac{y^k dy}{\sqrt{y-1}} = 2 \int_0^{\sqrt{3}} (1+z^2)^k dz =$$

$$= 2\sqrt{3} \left\{ 1 + k \frac{3}{3} + \frac{k(k-1)}{2!} \frac{3^2}{5} + \frac{k(k-1)(k-2)}{3!} \frac{3^3}{7} + \dots \right\}$$

So we find for E a series of the following form :

$$E = - \frac{tc^2}{\sqrt{3}} \left\{ \frac{p_1}{3!} + \frac{2c^2}{5!} p_2 + \frac{3c^4}{7!} p_3 + \dots \right\}$$

the coefficients p having the following values :

$$p_1 = 2\sqrt{3}.2$$

$$p_2 = 2\sqrt{3} \frac{2^2 \cdot 6}{5}$$

$$p_3 = 2\sqrt{3} \frac{4^2 \cdot 29}{5 \cdot 7}$$

$$p_4 = 2\sqrt{3} \frac{6^2 \cdot 602}{5 \cdot 7 \cdot 9}$$

$$p_5 = 2\sqrt{3} \frac{8^2 \cdot 700}{5 \cdot 7 \cdot 9 \cdot 11}$$

In order to investigate whether this series converges or not, we notice that in $\int_1^4 \frac{y^k dy}{\sqrt{y-1}}$ the factor $\sqrt{y-1}$ is always positive between the limits 1 and 4. So the value of the integral lies between the values: $y'_k \int_1^4 \frac{dy}{\sqrt{y-1}}$ and $y''_k \int_1^4 \frac{dy}{\sqrt{y-1}}$ where y' represents the minimum value and y'' the maximum value of y between the given limits. Here we have $y' = 1$ and $y'' = 4$. The value of the term of order k of the series for E lies therefore between the terms of order k of the two series :

$$E' = - 2t \left\{ \frac{c^2}{3!} + \frac{2c^4}{5!} + \frac{3c^6}{7!} \dots \right\}$$

and

$$E'' = - 2t \left\{ \frac{(2c)^2}{3!} + \frac{2 \cdot (2c)^4}{5!} + \frac{3 \cdot (2c)^6}{7!} \dots \right\}$$

and as the ratio between two consecutive terms of these series verges for terms of high degree to zero, the series for E will also converge.

Having determined the value of E , we find the law of attraction by changing the sign and differentiating with respect to r . Of course we must first replace c by $\frac{m^2}{3r^3 t}$. The value which we find for the force is negative; this indicates that the force represents an attraction, as we knew beforehand that we should find. The lowest degree of $1/r$ which occurs in the series is the seventh degree, therefore the force will vary more rapidly than proportional to $\frac{1}{r^7}$.

In connection with this result I wish to make the following remarks.

1st The law for the attraction which we should find on the supposition of vibrating double points whose distance is small compared with the wave length, will probably not differ very much from the law established here, though this question cannot as yet be answered with certainty.

2nd If we assume that m , without being periodical can yet increase or decrease under the influence of \mathcal{C} , then we find a still more rapid variation with r .

Also if we assume that the molecules are not simple double points but more complex configurations, quadruple or octuple points for instance, we find a more rapid variation with r . The double points assumed here seem to yield the slowest variation with r that we can find when we interpret the molecular forces by means of equal positive and negative electrical charges in the molecules. Much sooner, therefore, than to assert that the electron-theory supports the supposition of a molecular attraction proportional to $\frac{1}{r^4}$ we are justified in declaring that this supposition is excluded by the electron-theory.

3rd. If we assume m to be independent of the temperature T , then the attraction which we find, does, indeed, depend upon the temperature and that in such a way that at increasing temperature it decreases more rapidly than $\frac{1}{T}$. We have, however, no reason for supposing m to be independent of T ; moreover it makes here an enormous difference whether we are dealing with constant or with vibrating double points. It is therefore impossible to say whether the electric explanation of the molecular forces justifies us in assuming the attraction to increase or to decrease with T .

4th. We may wish to determine the shape of the equation of state which follows from the here assumed suppositions as to the action of the molecular forces. If we then follow the virial-method

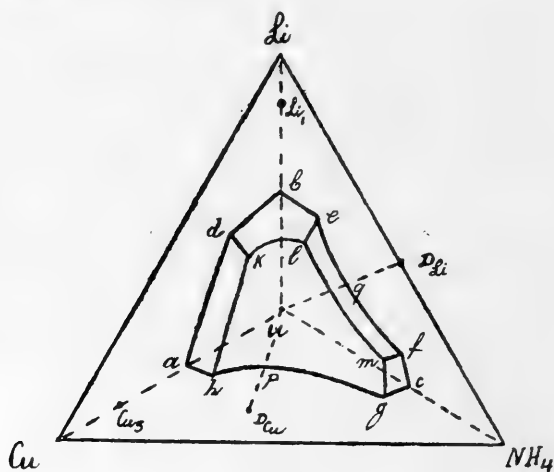
the virial of the resulting mean molecular attraction need only be taken into account. It is true that the molecules exercise on each other still other forces besides this mean attraction, but these forces yield a virial zero. The forces normal to the radius vector, namely form together a couple, and the virial of a couple is zero. For the same reason the directing couples working on the molecules need not be taken into account. And from the forces working in the direction of the radius vector we need only take into account the average value, for attracting and repulsing forces which equally often occur between different pairs of molecules, cancel each other.

In calculating the virial, the influence of the molecular attraction on the distribution in space of the molecules must of course still be taken into account.

Chemistry. — “*Equilibria in quaternary systems.*” By Prof. Dr. F. A. H. SCHREINEMAKERS.

In the system: Copper sulphate, ammonium sulphate, lithium sulphate and water two more solid compounds occur at 30° in addition to the three sulphates namely, $\text{Cu SO}_4 (\text{NH}_4)_2 \text{SO}_4 \cdot 6 \text{H}_2\text{O}$ and $\text{Li}_2 \text{SO}_4 (\text{NH}_4)_2 \text{SO}_4$.

We will again represent the equilibria in the wellknown manner with the aid of a tetrahedron but now choose quite a different projection than that used in the previous communication; we will in fact project all saturation lines and surfaces perpendicularly on one of the side planes of the tetrahedron.



A projection of this kind is represented in the figure; the points

Cu, Li, NH₄ and W indicate the four components Cu SO₄, Li₂ SO₄, (NH₄)₂ SO₄ and water; the triangle Cu Li NH₄ is the side plane on which all is projected. The dotted lines Cu W, Li W and NH₄ W are the projections of the rising sides of the tetrahedron and it is obvious that the point W must lie in the centre of the triangle.

The question is now what connection exists between the position of a point in the tetrahedron and its projection on the triangle Cu Li NH₄.

Let us take a phase with the composition: Cu proportions of Cu SO₄, Li proportions of Li₂ SO₄, N proportions of (NH₄)₂ SO₄ and W proportions of water. The projection of this point on the triangle Cu Li NH₄ may then be taken as indicating a phase which only contains the three components Cu SO₄, Li₂ SO₄ and (NH₄)₂ SO₄.

Let us call these proportions Cu', Li' and N'. It is now easily demonstrated that

$$\text{Cu}' = \text{Cu} + \frac{\text{W}}{3} \quad \text{Li}' = \text{Li} + \frac{\text{W}}{3} \quad \text{N}' = \text{N} + \frac{\text{W}}{3}$$

so that if the composition of a phase is known its projection may be readily represented in a drawing.

The double salt Li₂ SO₄. (NH₄)₂ SO₄ is represented in the figure by D_{Li}; it is obvious that it must be situated on the line Li NH₄ as it consists merely of the components Li₂ SO₄ and (NH₄)₂ SO₄. The double salt Cu SO₄. (NH₄)₂ SO₄. 6 H₂ O which contains three components must lie on the side plane W Cu NH₄ and is represented by D_{Cu}.

Both copper and lithium sulphate occur as hydrates, namely Cu SO₄. 5 H₂ O and Li₂ SO₄. H₂ O; they are represented in the figure by Cu₅ and Li₁; of course Cu₅ must lie on the side Cu W and Li on Li W.

Let us first consider the three ternary equilibria.

1. *Copper sulphate—ammonium sulphate—water.* The equilibria occurring in this system at 30° have been determined by Miss W. C. DE BAAT; the results of this investigation are represented by the saturation lines *ah*, *hpg*, and *gc*; *ah* indicates the solutions saturated with Cu SO₄. 5 H₂ O; *gc* is the saturation line of solid (NH₄)₂ SO₄ and *hpg* represents the solutions saturated with Cu SO₄. (NH₄)₂ SO₄. 6 H₂ O. As the line W D_{Cu} intersects the saturation line *hpg*, the double salt is soluble in water without decomposition; its solubility is represented by *p*.

2. *Lithium sulphate—ammonium sulphate—water.* The equilibria occurring in this system at 30° are represented by the saturation lines *be*, *eqf* and *fc*; the first is the saturation line of Li₂ SO₄. H₂ O;

the second that of the double salt $\text{Li}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$, the last that of $(\text{NH}_4)_2\text{SO}_4$. As the line W D_{Li} intersects the saturation line of the double salt it is soluble in water without decomposition.

As regards the branch *be* I stated that this indicates solutions which are in equilibrium with $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$; this is not quite correct for lithium sulphate, although only to the extent of a few %, gives mixed crystals with ammonium sulphate.

3. *Lithium sulphate—copper sulphate—water*. Whereas in the two previous ternary systems a double salt occurs, this is not the case in this system at 30° ; the isotherm therefore only consists of two branches; *ad* is the saturation line of $\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$ and *bd* that of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

These two branches have been determined by Mr. KOOPAL.

The quaternary equilibria at 30° are represented by surfaces, lines and points.

The surface *ahkd* is the saturation surface of $\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$; it therefore indicates the quaternary solutions which are saturated with $\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$.

The surface *dkleb* is the saturation surface of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

The surface *cfmg* is the saturation surface of $(\text{NH}_4)_2\text{SO}_4$.

The three surfaces observed are the saturation surfaces of the components or of their hydrates; in addition we also have the saturation surfaces of the double salts; that of $\text{Li}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ is represented by *elmfq*; that of $\text{Cu SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$ by *hklmgph*.

The saturation lines are formed by the intersection of the saturation surfaces taken two by two; they consequently represent solutions saturated with two solid substances.

We now see at once that solutions represented by the points of the lines:

<i>hk</i>	are saturated with	$\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$	and	D_{Cu}
<i>dk</i>	„ „ „	$\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$	and	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
<i>kl</i>	„ „ „	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	and	D_{Cu}
<i>le</i>	„ „ „	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	and	D_{Li}
<i>lm</i>	„ „ „	D_{Li}	and	D_{Cu}
<i>mf</i>	„ „ „	D_{Li}	and	$(\text{NH}_4)_2\text{SO}_4$
<i>mg</i>	„ „ „	D_{Cu}	and	$(\text{NH}_4)_2\text{SO}_4$

The quaternary saturation lines may be distinguished into external lines and middle lines; the external lines such as *kh*, *kd*, *le*, *mf* and *mg* each terminate in a point of a side plane, therefore in a ternary solution; the middle lines such as *kl* and *lm* are situated quite within the tetrahedron.

In each of the saturation points three saturation surfaces and therefore also three saturation lines meet each other; such a point therefore represents a solution saturated with three solid substances.

From this it follows that the solution represented:

by k is saturated with $\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$, $\text{Li}_2 \text{SO}_4 \cdot \text{H}_2\text{O}$ and D_{Cu}

„ l „ „ „ D_{Li} , $\text{Li}_2 \text{SO}_4 \cdot \text{H}_2\text{O}$ and D_{Cu}

„ m „ „ „ D_{Li} , $(\text{NH}_4)_2 \text{SO}_4$ and D_{Cu} .

This shows that each of these solutions is saturated with $\text{Cu SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6 \text{H}_2\text{O}$.

With the aid of this figure we may readily draw some conclusions. Let us therefore observe the external lines, for instance dk . The point d represents a ternary solution saturated at 30° with $\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$ and $\text{Li}_2 \text{SO}_4 \cdot \text{H}_2\text{O}$. To this solution we add $(\text{NH}_4)_2 \text{SO}_4$; the solution will now alter its composition until at last a third solid phase appears. What is this phase? $(\text{NH}_4)_2 \text{SO}_4$ forms a double salt with copper as well as with lithium sulphate and the question now arises which of these two will appear first. The experiment shows that $\text{Cu SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6 \text{H}_2\text{O}$ is formed. If we start from the ternary solution h which is saturated at 30° with $\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$ and $\text{Cu SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6 \text{H}_2\text{O}$ and if $\text{Li}_2 \text{SO}_4 \cdot \text{H}_2\text{O}$ is added the solution undergoes the changes represented by points of the line hk until finally the third solid phase occurs in k in this case $\text{Li}_2 \text{SO}_4 \cdot \text{H}_2\text{O}$.

If we start from the ternary solution f saturated at 30° with $(\text{NH}_4)_2 \text{SO}_4$ and $\text{Li}_2 \text{SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4$ and if we add $\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$ and represent the solution by m $\text{Cu SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6 \text{H}_2\text{O}$ is formed as the third solid phase; if we start from the ternary solution g which is saturated with $(\text{NH}_4)_2 \text{SO}_4$ and $\text{Cu SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6 \text{H}_2\text{O}$ and add $\text{Li}_2 \text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{Li}_2 \text{SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4$ will form in m as the third phase.

If we start from the ternary solution e which is saturated with $\text{Li}_2 \text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{Li}_2 \text{SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4$ and add $\text{Cu SO}_4 \cdot 5 \text{H}_2\text{O}$ the solution traverses the branch el ; in l however a new solid phase is formed, namely, $\text{Cu SO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6 \text{H}_2\text{O}$.

Suppose a plane is passed through the points W , Cu and D_{Li} of the tetrahedron; the points of this plane represent solutions with a constant proportion of the components $\text{Li}_2 \text{SO}_4$ and $(\text{NH}_4)_2 \text{SO}_4$; this ratio is the same as that in which they occur in the double salt. This plane intersects the saturation surface $leqfm$ of this double salt, so that this is not only soluble without decomposition in water but also in solutions of copper sulphate of a definite concentration.

In order to find the composition of the solid phases which can be in equilibrium with definite solutions I have acted in the same manner as I did previously with ternary systems; I have applied the "residue-method".

If the solution is in equilibrium with one solid substance the conjugation line solution-residue must pass through the point indicating this solid substance; if it is in equilibrium with two solid substances the conjugation line solution-residue intersects the communication line of the two solid substances and if it is in equilibrium with three solid substances it intersects the triangle which has those three solid substances as its angular points.

These constructions are much facilitated by taking a rectangular tetrahedron instead of an equilateral one and projecting the whole on two of the side planes.

Astronomy. — "*The investigation of the weights in equations according to the principle of the least squares*". By J. WEEDER.
(Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN).

When results of measurement deduced from different modes of measuring or originating from different observers are equated mutually, it is generally advisable to test the weights assigned to these results, before equating, with the apparent errors produced by the equation in order to be able to judge whether it is necessary to correct them and to distinguish in what direction correction is obtained. Let the material of observation break up according to its origin into groups and let out of the apparent errors of each group separately the mean error of the unity of weight be deduced, then it is a necessity for the differences of those values to be small, at least they may not overstep the limits which can be fixed taking into account the numbers of apparent errors in each group.

Already at the outset of such investigations the problem thus appears how the mean error of the unity of weight can be calculated, if one wishes to use but a part of the apparent errors.

When equating determinations of errors of division of the Leyden meridian circle I have applied the following formula:

$$\mu = \sqrt{\frac{\sum gf^2}{n-k}}$$

Here

μ = the mean error of unity of weight,
 g = the weight of a result of observation,

f = the apparent error calculated for this result,

n = the number of errors out of the group,

k = a number depending on the weights of the results of measurement and on the coefficients the unknown quantities, determined by the equating, are associated with in the equations expressing the connection between these unknown quantities and the results of measurement of the group.

In what way k is dependent on the above-mentioned quantities will become clear by an example for which I choose the case that 3 unknown quantities x, y, z are determined by N equations of the form $ax + by + cz = l$, whilst to the quantities l appearing in this equation and obtained by measurement the weights g are due. In this case

$$k = \sum g (a^2 Q_{xx} + 2ab Q_{xy} + b^2 Q_{yy} + 2ac Q_{xz} + 2bc Q_{yz} + c^2 Q_{zz})$$

where the summations in the formulae for k and μ include expressions relating to the same results of measuring. In the above formula the quantities Q , the well-known numbers of weight, can be calculated by means of the coefficients of the normalequations.

For the deduction of this formula we have the same considerations which lead to the mean error of the unity of weight out of *all* observations. If the real errors are indicated by h then $n\mu^2 = \sum gh^2$; this sum is expressed in the apparent errors that can be calculated, and in the errors $\Delta x, \Delta y$ and Δz of the quantities x, y and z , calculated out of the normal equations, by means of the relation $h = f + a\Delta x + b\Delta y + c\Delta z$, so that

$$\begin{aligned} n\mu^2 = & \sum gf^2 + 2(\Delta x \sum gfa + \Delta y \sum gfb + \Delta z \sum gfc) + \\ & + (\Delta x)^2 \sum ga^2 + 2(\Delta x)(\Delta y) \sum' gab + (\Delta y)^2 \sum' gb^2 + \\ & + 2(\Delta x)(\Delta z) \sum' gac + 2(\Delta y)(\Delta z) \sum' gbc + (\Delta z)^2 \sum' gc^2 \end{aligned}$$

If we were to use the whole material of errors, then the first three of the unknown terms would fall out on account of $[gfa] = 0$, $[gfb] = 0$ and $[gfc] = 0$. (Here and for the future I make use of $[\]$ as sign of a summation extending over *all* observations). To take as well as possible the unknown terms in the above into account we replace them by their mean values in the supposition that the same complex of observations repeats itself manifold times so that all calculable quantities return unmodified in each repetition. In that supposition $\Delta x, \Delta y$ and Δz have zero as mean values and the mean values of their squares and products are in the above order :

$$Q_{xx} \mu^2, Q_{xy} \mu^2, Q_{yy} \mu^2, Q_{xz} \mu^2, Q_{yz} \mu^2 \text{ and } Q_{zz} \mu^2$$

If we connect these mean values having μ^2 as factor with the term

$n\mu^2$ in the above equation, if we put

$$\sum g (a^2 Q_{xx} + 2abQ_{xy} + b^2 Q_{yy} + 2acQ_{xz} + 2bcQ_{yz} + c^2 Q_{zz}),$$

equal to k and if we solve μ out of the equation, we obtain

$$\mu = \sqrt{\frac{\sum g f^2}{n-k}}, \text{ i. e. the formula of which I made use to determine}$$

the mean error of the unity of weight out of a particular group of apparent errors.

I arrived at *about* the same result by another consideration putting to myself the problem to determine the mean value M_{f_i} of a definite apparent error f_i . In the relation :

$$f_i = l_i - a_i x - b_i y - c_i z$$

I substituted for x, y, z respectively $[a'l], [\beta'l], [\gamma'l]$ to obtain f_i in the form of a linear expression of the results of measuring l which are supposed to be quite independent of each other.

Then :

$$M^2_{f_i} = \left\{ 1 - 2(a_i \alpha_i + b_i \beta_i + c_i \gamma_i) \right\} \frac{\mu^2}{g_i} + \left[(a_i \alpha + b_i \beta + c_i \gamma)^2 \frac{\mu^2}{g} \right].$$

It would now be the only way of reduction of this equation to make use of the well-known relations existing between the coefficients α, β, γ and a, b, c and the numbers of weight Q , namely :

$$\alpha = g (a Q_{xx} + b Q_{xy} + c Q_{xz}),$$

$$\beta = g (a Q_{xy} + b Q_{yy} + c Q_{yz}),$$

$$\gamma = g (a Q_{xz} + b Q_{yz} + c Q_{zz}),$$

in order to prove that

$$\left[(a_i \alpha + b_i \beta + c_i \gamma)^2 \frac{1}{g} \right] = \frac{a_i \alpha_i + b_i \beta_i + c_i \gamma_i}{g_i}.$$

I propose however to deduce this equation directly from the minimum condition :

$$[g (l - ax - by - cz)^2] = \text{minimum.}$$

If here too x, y, z are replaced by $[a'l], [\beta'l]$ and $[\gamma'l]$, then after calculation and combination of the equal powers and products of the quantities l an expression appears of the form $\sum \sum C_{\mu}^{\nu} l_{\mu} l_{\nu}$, having for the right set of coefficients α, β, γ a minimum value. I observe here that the coefficients α, β, γ have to satisfy the minimum condition independently of the particular values which the measurements furnished for the quantities l . Out of this observation ensues that the partial derivatives of C_{μ}^{ν} with respect to each of the coefficients α, β, γ furnish zero by substitution of the right values of these coefficients.

By calculation and arrangement of the terms of the minimum condition we arrive at

$$C'_\mu = 2 [g(a\alpha_\mu + b\beta_\mu + c\gamma_\mu)(a\alpha_\nu + b\beta_\nu + c\gamma_\nu)] - \\ - 2g_\mu(a_\mu\alpha_\nu + b_\mu\beta_\nu + c_\mu\gamma_\nu) - 2g_\nu(a_\nu\alpha_\mu + b_\nu\beta_\mu + c_\nu\gamma_\mu)$$

The expression $[g(a\alpha_\mu + b\beta_\mu + c\gamma_\mu)(a\alpha_\nu + b\beta_\nu + c\gamma_\nu)]$ being put equal to F , the conditions for the minimum furnish the following equations :

$$\frac{\partial F}{\partial \alpha_\mu} = g_\nu a_\nu \frac{\partial F}{\partial \beta_\mu} = g_\nu b_\nu \frac{\partial F}{\partial \gamma_\mu} = g_\nu c_\nu, \\ \frac{\partial F}{\partial \alpha_\nu} = g_\mu a_\mu \frac{\partial F}{\partial \beta_\nu} = g_\mu b_\mu \frac{\partial F}{\partial \gamma_\nu} = g_\mu c_\mu.$$

Such an expression F which, as far as the coefficients α , β , γ appear in it, contains only products of one of the $\alpha_\mu \beta_\mu \gamma_\mu$ with one of the $\alpha_\nu \beta_\nu \gamma_\nu$ can be written as linear expression in each of those sets of 3 coefficients in the following way :

$$F = \alpha_\mu \frac{\partial F}{\partial \alpha_\mu} + \beta_\mu \frac{\partial F}{\partial \beta_\mu} + \gamma_\mu \frac{\partial F}{\partial \gamma_\mu} = \alpha_\nu \frac{\partial F}{\partial \alpha_\nu} + \beta_\nu \frac{\partial F}{\partial \beta_\nu} + \gamma_\nu \frac{\partial F}{\partial \gamma_\nu}.$$

So that by substituting the equations resulting from the minimum we arrive at the following relations :

$$F = g_\nu(a_\nu\alpha_\mu + b_\nu\beta_\mu + c_\nu\gamma_\mu) = g_\mu(a_\mu\alpha_\nu + b_\mu\beta_\nu + c_\mu\gamma_\nu).$$

In words this relation runs: with equal weights an error in l_μ has equal influence on the apparent error f_ν as an equally large error in l_ν has on the apparent error f_μ . If the weights of the two results of measuring are unequal, errors in these which are in inverse ratio with their weights will cause each other's apparent errors to deviate to the same amount from the true ones.

Let us put in the condition

$$[g\{l - a[a] - b[\beta] - c[\gamma]\}^2] = \text{minimum}$$

$l_i = 1$ and all other quantities $l = 0$, then from this arises

$$g_i(1 - 2a_i\alpha_i - 2b_i\beta_i - 2c_i\gamma_i) + [g(a\alpha_i + b\beta_i + c\gamma_i)^2] = \text{min.}$$

from which we deduce putting $[g(a\alpha_i + b\beta_i + c\gamma_i)^2] = G$:

$$\frac{\partial G}{\partial \alpha_i} = 2g_i\alpha_i \quad \frac{\partial G}{\partial \beta_i} = 2g_ib_i \quad \frac{\partial G}{\partial \gamma_i} = 2g_ic_i$$

and from this ensues again :

$$G = \frac{1}{2}\alpha_i \frac{\partial G}{\partial \alpha_i} + \frac{1}{2}\beta_i \frac{\partial G}{\partial \beta_i} + \frac{1}{2}\gamma_i \frac{\partial G}{\partial \gamma_i} = g_i(a_i\alpha_i + b_i\beta_i + c_i\gamma_i).$$

With the aid of the above deduced theorem each term of the summation in the expression $[g(a\alpha_i + b\beta_i + c\gamma_i)^2]$ can be replaced

by a corresponding one in which the constant index i is given to the coefficients a, b, c , so we have:

$$G = \left[\frac{g_i^2}{g} (a_i \alpha + b_i \beta + c_i \gamma)^2 \right] = g_i (a_i \alpha_i + b_i \beta_i + c_i \gamma_i)$$

from which results after division by g_i^2 the relation I was to prove.

Using this relation I find:

$$M_h^2 = (1 - a_i \alpha_i - b_i \beta_i - c_i \gamma_i) \frac{\mu^2}{g_i}$$

If we call $a \alpha + b \beta + c \gamma = z$, then $f \sqrt{\frac{g}{1-z}}$ can be calculated out of each apparent error and the mean value of this system of errors is equal to μ , as that of the system of unknown errors is $h \sqrt{g}$. It therefore seems to me not only permissible, but for a test of the weights even useful, to make use of that system of errors which allows the mean error of the unity of weight to be deduced out of each definite part of these errors. The connection between the quantities z and the number k of the above formula applied by me can be indicated by the relation $\Sigma z = k$.

Physics. - "*Contribution to the theory of binary mixtures*". VII.

By Prof. J. D. VAN DER WAALS.

ON THE RELATION BETWEEN THE QUANTITIES a_{12} AND a_1 AND a_2 , WHICH OCCUR IN THE THEORY OF A BINARY MIXTURE.

I have already frequently traced the course of the thermodynamic curves for the case that for a binary system minimum plaitpoint temperature occurs, and so also the quantity $\frac{a_x}{b_x}$ has a minimum value for certain value of x . Both the course of the isobars and the course of the lines $\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$ may be assumed as known for that case. And experiment has shown that the shape of these lines predicted by theory it at least qualitatively accurate.

I purpose to demonstrate in these pages that in the case mentioned the course of these lines (see among others fig. 1 page 626 Vol. IX of these Proceedings 1907) is not compatible with the supposition $a_{12}^2 = a_1 a_2$.

I begin with pointing out that the line $\left(\frac{dp}{dx}\right)_v = 0$ has an asymptote for such a value of x for which $MRT \frac{db}{dx} = \frac{da}{dx}$, which asymptote either exists or must be supposed to exist for a value of x which is negative, and that this curve approaches the line $v = b$ asymptotically for continually increasing values of x — at least if $a_1 + a_2 - 2a_1$, is positive. I shall presently come back to this supposition, but on page 626 I have explicitly stated this supposition in the form $\frac{d^2a}{dx^2}$ positive. With increase of T this line proceeds to higher value of x and v .

At lower temperatures the line $\left(\frac{dp}{dv}\right)_x = 0$ consists of two separate branches. From $\frac{d^2p}{dv^2} \frac{dv}{dx} + \frac{d^2p}{dx dv} = 0$ follows that the liquid branch has maximum volume on the line $\frac{d^2p}{dx dv} = 0$ and the vapour branch minimum volume on the same curve, which curve has an analogous course to $\left(\frac{dp}{dx}\right)_v = 0$. It has the same asymptotes, but is always confined to greater volume. For $T =$ minimum critical temperature the two branches coincide in a point for which both $\frac{d^2p}{dv^2}$ and $\frac{d^2p}{dx dv}$ is equal to 0, so in such a point of the line $\frac{d^2p}{dx dv} = 0$, for which $\left(\frac{dp}{dv}\right)_x = 0$ and also $\frac{d^2p}{dv^2} = 0$. Hence in the critical point of the mixture taken as homogenous, for which $\frac{a_x}{b_x}$ has minimum value. At still higher value of T the curve $\left(\frac{dp}{dv}\right)_x = 0$ has split up into a lefthand branch and a righthand branch, both which branches possess tangents parallel to the v -axis, in points for which also $\left(\frac{dp}{dv}\right)_x = 0$ and $\frac{d^2p}{dv^2} = 0$. Among the special values of this constantly increasing value of T we must mention in the first place that for which the last mentioned point has got on the line $\left(\frac{dp}{dx}\right)_v = 0$, the point P of fig. 31. This is the

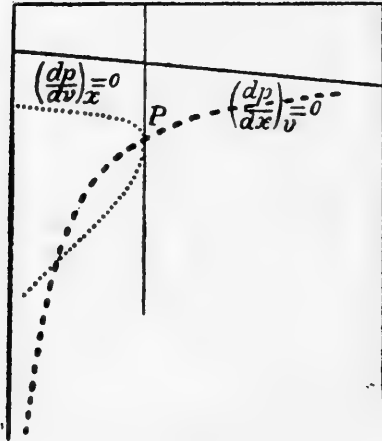


Fig. 31.

remarkable point for which *plaitpoint* and *critical point of the mixture* taken as homogeneous coincide. So at this temperature the two curves $\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$ still intersect in two points. The other point of intersection lies, of course, at greater volume. With further rise of temperature the two curves contract further. The line $\left(\frac{dp}{dv}\right)_v = 0$

the right and the line $\left(\frac{dp}{dv}\right)_x = 0$ to the left. At a certain temperature these two curves touch, and at still higher temperature they have got quite detached. This point of contact of the two curves lies, of course, on the vapour branch of $\left(\frac{dp}{dv}\right)_x = 0$, and so has a greater volume than the critical volume.

We can calculate the volume in case of contact. The condition of contact of $\left(\frac{dp}{dv}\right)_x = 0$ and $\left(\frac{dp}{dx}\right)_v = 0$ is given by equal value of $\frac{dv}{dx}$ in the two following equations:

$$\frac{d^2p}{dv^2} \frac{dv}{dx} + \frac{d^2p}{dx dv} = 0$$

and

$$\frac{d^2p}{dx dv} \frac{dv}{dx} + \frac{d^2p}{dx^2} = 0$$

or from:

$$\frac{d^2p}{dv^2} \frac{d^2p}{dx^2} = \left(\frac{d^2p}{dx dv}\right)^2 \quad (\text{see p. 691}).$$

This latter equation and the two equations $\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$ form a set of three which is sufficient for the determination of the three quantities x , v and T of the point of contact. If we assume b to be constant in the equation of state these equations have the following form:

$$\left[\frac{MRT}{(v-b)^3} - \frac{3a}{v^4} \right] \left[\frac{MRT \left(\frac{db}{dx}\right)^2}{(v-b)^3} - \frac{1}{2} \frac{d^2a}{v^2} \right] = \left[\frac{MRT}{(v-b)^3} \frac{db}{dx} - \frac{da}{v^3} \right]^2 \quad \dots \quad (1)$$

$$\frac{MRT}{(v-b)^2} \frac{db}{dx} = \frac{da}{dx} \frac{1}{v^2} \dots \dots \dots (2)$$

and

$$\frac{MRT}{(v-b)^2} = \frac{2a}{v^2} \dots \dots \dots (3)$$

If now we make use of (2) and (3) for the elimination of MRT and of $\frac{db}{dx}$, we get a simple form for $\frac{v}{b}$, viz.:

$$\frac{v}{b} = \frac{3a \frac{d^2a}{dx^2} - 2 \left(\frac{da}{dx}\right)^2}{a \frac{d^2a}{dx^2} - \left(\frac{da}{dx}\right)^2} \dots \dots \dots (4)$$

We may also get a quadratic equation in $\frac{v}{b}$, but then it appears that one of the values of $\frac{v}{b} = 1$, and that at $T = 0$ the line $v = b$ may be considered as coinciding with the branch of the volumes of $\left(\frac{dp}{dv}\right)_x = 0$, and also with $\left(\frac{dp}{dx}\right)_v = 0$. In the same way the line $v = \infty$.

If we now write for the ratio of $\left(\frac{da}{dx}\right)^2$ and $a \frac{d^2a}{dx^2}$ the quantity m ,

so that $m = \frac{\left(\frac{da}{dx}\right)^2}{a \frac{d^2a}{dx^2}}$ then (4) becomes:

$$\frac{v}{b} = \frac{3-2m}{1-m}$$

And drawing $\frac{v}{b}$ as ordinate when m is laid out along the axis of the abscissae, we get fig. 32. For $m = 0$ we have $\frac{v}{b} = 3$ and for $m = 1$ we have $\frac{v}{b} = \infty$. For $m > 1$ $\frac{v}{b}$ is at first negative, but for $m = \frac{3}{2}$, $\frac{v}{b} = 0$, and for greater values of m $\frac{v}{b}$ is positive and steadily increasing. The limiting value is $\frac{v}{b} = 2$. For negative value of m $\frac{v}{b}$ is always positive, descending from $\frac{v}{b} = 3$ to $\frac{v}{b} = 2$. The

traced curve is an equilateral hyperbola. So a value of $\frac{v}{b}$ larger than 3 is possible only when v lies between 0 and 1. Thus $\frac{v}{b} = 4$ requires a value of $m = 1/2$.

Accordingly it is impossible to account for a minimum plaitpoint temperature of substances for which m does not lie between 0 and 1.

Now I have already repeatedly called attention to the equation:

$$2a \frac{d^2 a}{dx^2} = \left(\frac{da}{dx} \right)^2 + 4(a_1 a_2 - a_{1,2}^2),$$

which follows from the supposition that a is a quadratic form of x , and already in my Molecular Theory for a binary mixture I pointed out, realizing the desirability of a relation being found between $a_{1,2}$ and a_1 and a_2 , that the equation of the spinodal line for a binary mixture might be very much simplified if we were justified in assuming $a_{1,2}^2 = a_1 a_2$. I also pointed out other relations between these quantities; but I have carefully refrained from even giving so much as the slightest indication of the greater probability of one relation. I have only repeatedly, then and later, assumed as relation for mixtures with minimum plaitpoint temperature $a_1 + a_2 > 2a_{1,2}$, and reversely, when also mixtures with maximum plaitpoint temperature might occur: $a_1 + a_2 < 2a_{1,2}$. And I have repeatedly pointed out that there is no reason whatever for putting e. g. $a_{1,2}^2 = a_1 a_2$. And to this the following considerations have chiefly led me.

In the equation of state for a simple substance the two constants b and a have not been introduced on equally sufficient grounds and with the same certainty. To the existence of the quantity b we conclude with perfect certainty if we believe that to occupy space is an essential property of matter. Even MAXWELL, who would not attribute a volume of their own to the molecules, but wanted to consider them as so-called material points, understanding that collisions could not take place between material points, could not but attribute to them at least an apparent volume. By assuming a repulsive force he had to account for their never meeting, and for their behaviour as particles possessing impermeability on approaching each other with reversal of motion. A hypothesis whose improbability is not to be denied. The force would be a repulsive one, and probably in inverse ratio to the fifth power of the distance. How and why the attraction at somewhat larger distance is converted into such a repulsive force is a question that was probably never put by him,

and at all events was not answered by him. So the introduction of the quantity b into the equation of state is perfectly natural — and for everybody who assumes the existence of matter as real, indispensable. But this is not, at least not in the same degree, the case with the quantity a . Why should molecular attraction be a necessary attribute of matter? From the idea: “matter is something that necessarily occupies space” does not follow that matter will also have to possess attraction. Perhaps we shall sooner or later learn to form a conception on the nature of a molecule which involves that they necessarily attract each other and learn to compute the value of this attraction. Of late attempts have therefore been made to get a better insight into the nature of molecules, and they are supposed to be either vibrating or permanent electrical double points¹⁾. But even if this supposition appeared to account satisfactorily for the molecular attraction, yet it does not necessarily follow that attraction exists. Then the question has changed in so far that it runs: are there electrical double points in the molecule or not? It is true that in my Thesis for the Doctorate (1873) p. 92, when the question occurred whether hydrogen possesses a critical temperature I answered in the sense of a high degree of probability, but only on a ground which leaves some room for doubt, viz. that “It may be presumed that matter will always have attraction”. It is not to be denied that everything that we accept as matter is subjected to gravity; but to derive from this that the existence of the NEWTONIAN attraction involves the possession of molecular attraction is more than hazardous. All this is not intended to raise doubt about the existence of a e. g. for helium, for now that all other substances possess a value for a we may repeat what I said before for hydrogen, but to draw attention to the fact that the value of a does not only depend on the molecular weight. If this *was* the case, $\frac{a_1}{m_1^2} = \frac{a_2}{m_2^2}$, a relation which is certainly not fulfilled. Then also $\frac{a_1}{m_1^2} = \frac{a_2}{m_2^2} = \frac{a_{12}}{m_1 m_2}$, and $a_{12}^2 = a_1 a_2$, which very probably will never be fulfilled either.

I was convinced from the outset that we should not be able to explain a number of phenomena occurring for binary mixtures by means of such an unfounded supposition. Already a long time ago KORTEWEG showed in his paper “La surface ψ dans le cas de symétrie” in how high a degree the phenomena exhibited by a binary mixture, depend on the value ascribed to a_{12} . For values of a_{12} , between

1) See these Proc. p. 132.

certain limits not only three phase equilibrium but even four phase equilibrium would be possible, then of course always at a single value of T . So the supposition $a_1,^2 = a_1 a_2$ is not one without far-reaching consequences. Yet we see repeatedly that this supposition is made. And I have undertaken this investigation to show that such a supposition would also render the existence of minimum plaitpoint temperature impossible. At the same time I wanted to point out how the course of the isobars which I have given in fig. 1 of these contributions would be entirely modified on other suppositions about a_1 , than those I have started from. If we put in equation:

$$2a \frac{d^2 a}{dx^2} = \left(\frac{da}{dx} \right)^2 + 4(a_1 a_2 - a_{1,2}^2)$$

for $\left(\frac{da}{dx} \right)^2$ the value $m a \frac{d^2 a}{dx^2}$ in which, if there is minimum plaitpoint temperature the value of m lies between 0 and 1 for the point of contact of $\left(\frac{dp}{dx} \right)_v = 0$ and $\left(\frac{dp}{dv} \right)_x = 0$, we find:

$$\left(\frac{2}{m} - 1 \right) \left(\frac{da}{dx} \right)^2 = 4(a_1 a_2 - a_{1,2}^2)$$

$$(2 - m) a \frac{d^2 a}{dx^2} = 4(a_1 a_2 - a_{1,2}^2)$$

Now $\frac{d^2 a}{dx^2} = 2(a_1 + a_2 - 2a_{1,2})$. As at the same time we cannot have $a_1 a_2 = a_{1,2}^2$ and $a_1 + a_2 = 2a_{1,2}$, unless in the case $a_1 = a_2$, this equation cannot be fulfilled but by putting $a_1 a_2 > a_{1,2}^2$.

The supposition $a_1 a_2 = a_{1,2}^2$ gives for m the value 2, but then also for $\frac{v}{b}$ in the point of contact of $\left(\frac{dp}{dx} \right)_v = 0$ and $\left(\frac{dp}{dv} \right)_x = 0$, the value 1 (see fig. 32). — Only when we put $a_1 a_2 < a_{1,2}^2$ does m become > 2 , and do we find for the point of contact of the curve mentioned, values of $\frac{v}{b}$ which are larger than 1, and which can therefore exist, but then this value can rise to 2 at the utmost. In such cases there is contact of $\left(\frac{dp}{dx} \right)_v = 0$ with the liquid branch of $\left(\frac{dp}{dv} \right)_x = 0$. And this means for fig. 1 of these contributions that then again the liquid branch of $\left(\frac{dp}{dv} \right)_x = 0$ may approach to $\left(\frac{dp}{dx} \right)_v = 0$ on the right side, but then to that part of this curve that lies beyond the minimum

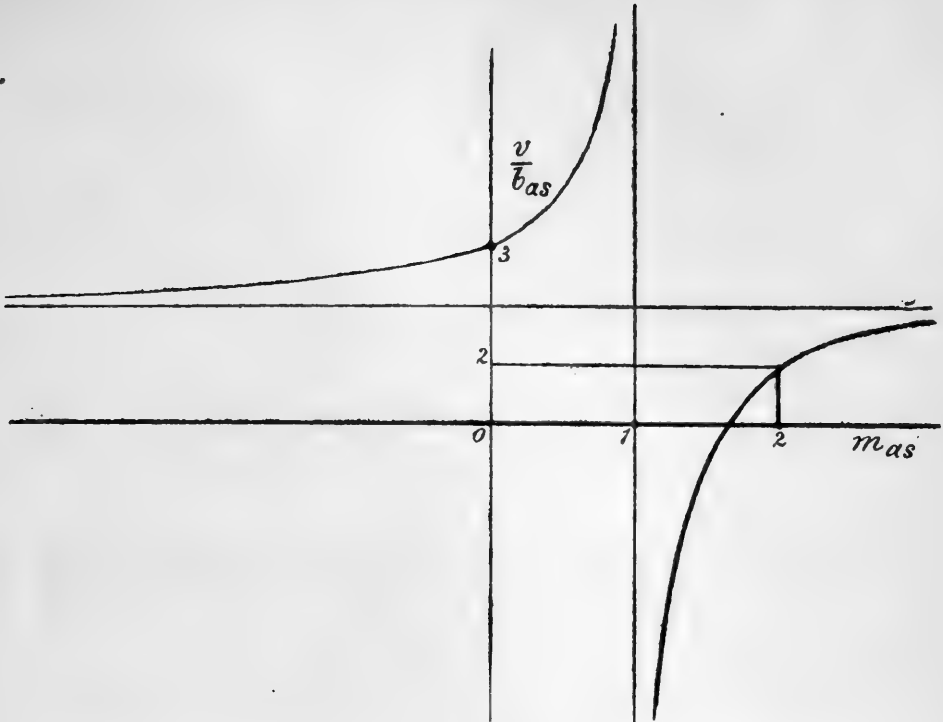


Fig. 32.

volume, and where it proceeds again to greater volumes. On the supposition that $a_{1,2}$ might rise above $a_1 a_2$, fig. 1 would not represent all possible cases of the course of the isobars with respect to $\left(\frac{dp}{dx}\right)_v = 0$. But I observed already on page 630 in what way fig. 1 would have to be extended if other suppositions on $a_1 + a_2 - 2a_{1,2}$ are admitted e. g. $a_1 + a_2 - 2a_{1,2} = 0$ or $a_1 + a_2 - 2a_{1,2}$ negative, and the supposition $a_1 a_2 < a_{1,2}^2$ lies in this direction.

If we continue increasing $a_{1,2}$, not only above $\sqrt{a_1 a_2}$, but even above $\frac{a_1 + a_2}{2}$, then $m = \frac{\left(\frac{da}{dx}\right)}{a \frac{d^2 a}{dx^2}}$ is negative, and $\frac{v}{b}$ lies between 2

and 3 for the point of contact of $\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$, and so this point of contact always lies on the liquid branch of $\left(\frac{dp}{dv}\right)_x = 0$.

We might also have arrived at the above results by another course, which would give us an opportunity of making some new remarks. For if we think the quantity v eliminated from the two equations

$\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$, we obtain a relation between x and T . In general we find two values of x for the same value of T . The value of T , at which these values of x coincide, or in other words, the maximum value of T , then gives us the value of x for the point of contact of the two curves.

From

$$\frac{MRT}{(v-b)^2} = \frac{2a}{v^3}$$

and

$$\frac{MRT}{(v-b)^2} \frac{db}{dx} = \frac{1}{v^2} \frac{dv}{dx}$$

we find

$$2 \frac{db}{dx} \frac{da}{a} = \frac{da}{a} \text{ for a point of intersection. . . (6)}$$

As for values of v which will be realisable, $v > b$ and v must be positive, a point of intersection of the two curves can only occur if

$\frac{da}{dx}$ is positive, and if $\frac{da}{a} < 2 \frac{db}{dx}$. This latter condition may be written

$\frac{d \frac{a}{b^2}}{dx} < 0$. So the two curves can never intersect in a region of increasing critical pressure. Let us therefore confine ourselves to decreasing critical pressure. The locus (6) has as differential equation:

$$- \frac{2 \frac{db}{dx} \frac{dv}{v^2} \frac{da}{a}}{\frac{d^2 a}{dx^2}} = \frac{a \frac{d^2 a}{dx^2} - \left(\frac{da}{dx}\right)^2}{a^2} (7)$$

So when $m = \frac{\left(\frac{da}{dx}\right)^2}{a \frac{d^2 a}{dx^2}} < 1$, $\frac{dv}{dx}$ is negative. Only in a region where

m has become $= 1$, $\frac{dv}{dx}$ will be positive. And if we should assume $a_1 a_2 = a_{12}^2$, so if we put $m = 2$, the locus of the points of intersection of the two curves would move to greater volume with increasing x ; so perfectly different from what happens for mixtures with minimum plaitpoint temperature. If we substitute the value of v which follows from (6), in:

$$MRT = \frac{2a}{b} \frac{b}{v} \left(1 - \frac{b}{v}\right)^2$$

we get:

$$MRT = \frac{a}{b} \frac{1}{\frac{1}{b} \frac{da}{dx}} \left\{ 1 - \frac{1}{\frac{2a}{b} \frac{da}{dx}} \right\}^2 \dots \dots \dots (7)$$

For values of x for which $\frac{da}{dx} = 0$ and $\frac{2}{b} \frac{db}{dx} = \frac{1}{a} \frac{da}{dx}$ or $\frac{d \log \frac{a}{b^2}}{dx} = 0$, the value of $T = 0$. Thus the same value of T always belongs to a couple of values of x which approach each other. And at the maximum value of T the two values of x have coincided. By differentiating (7) we get an equation which may be written in the form:

$$\frac{2a}{b} \frac{db}{dx} = \frac{3a \frac{d^2a}{dx^2} - 2 \left(\frac{da}{dx}\right)^2}{a \frac{d^2a}{dx^2} - \left(\frac{da}{dx}\right)^2} \frac{da}{dx}$$

from which, taking (6) into consideration, we obtain again (4).

It appears from the foregoing that putting $a_{1,2}^2 = a_1 a_2$ comes to the same thing as putting $m = 2$. For mixtures with minimum plait-point the value of m differs much from this value, as it is then smaller than 1, and so $a_{1,2}^2$ will have to differ pretty much from $a_1 a_2$. If we put $a_{1,2}^2 = l^2 a_1 a_2$, in which $l^2 < 1$, we find from:

$$2a \frac{d^2a}{dx^2} = \left(\frac{da}{dx}\right)^2 + 4(1-l^2) a_1 a_2$$

$$(2-m) a \frac{d^2a}{dx^2} = 4(1-l^2) a_1 a_2$$

or

$$\left(1 - \frac{m}{2}\right) (a_1 + a_2 - 2a_{1,2}) a = (1-l^2) a_1 a_2$$

It may be derived from this equation that m may lie near 2, even when l differs comparatively much from 1.

The value of a varying with x , also the ratio of $1 - \frac{m}{2}$ and $1-l^2$ will vary with x . If we make a increase with x , which probably will be in general the case, then a_1 is the smallest value of a and

a_2 the greatest value, whereas the value of a for $x = \frac{1}{2}$ will be equal to $\frac{a_1 + a_2 + 2a_{12}}{4}$.

So the ratio $\frac{1 - \frac{m}{2}}{1 - l^2}$ is for $x = 0$, $x = \frac{1}{2}$ and $x = 1$:

$$\frac{1 - \frac{m}{2}}{1 - l^2} = \frac{a_2}{a_1 + a_2 - 2a_{12}} = \frac{\frac{a_2}{a_1}}{\left(\sqrt{\frac{a_2}{a_1}} - 1\right)^2 + 2(1-l)\sqrt{\frac{a_2}{a_1}}}$$

$$\frac{1 - \frac{m}{2}}{1 - l^2} = \frac{4a_1 a_2}{(a_1 + a_2)^2 - 4a_{12}^2} = \frac{4\frac{a_2}{a_1}}{\left(\frac{a_2}{a_1} - 1\right)^2 + 4(1-l^2)\frac{a_2}{a_1}}$$

$$\frac{1 - \frac{m}{2}}{1 - l^2} = \frac{a_1}{a_1 + a_2 - 2a_{12}} = \frac{1}{\left(\sqrt{\frac{a_2}{a_1}} - 1\right)^2 + 2(1-l)\sqrt{\frac{a_2}{a_1}}}$$

If we choose the second of these equations, from which it is easiest to draw conclusions with regard to the value of m at given value of l^2 , we write it first in the following form:

$$\frac{2}{m} - 1 = \frac{4(1-l^2)\frac{a_2}{a_1}}{\left(\frac{a_2}{a_1} - 1\right)^2}$$

If we always take the same value of $1 - l^2$, but different values of $\frac{a_2}{a_1}$, we find very great differences in the value of m . For instance

with $\frac{a_2}{a_1} = 2$ we have $\frac{2}{m} - 1 = 8(1 - l^2)$, or $m = \frac{2}{1 + 8(1 - l^2)}$; but

with $\frac{a_2}{a_1} = 11$, m is found equal to $m = \frac{2}{1 + 0,44(1 - l^2)}$. With $l^2 = 1$

we find of course in both cases $m = 2$. But for smaller values of l the values of m differ considerably. For $l = 0$ these values are

$\frac{2}{9}$ and $\frac{2}{1,44}$.

If we had discussed the third of the equations, the values of m would have been found still higher. According to the first of the equations of course smaller.

Let us finally examine the course of the line $\left(\frac{dp}{dx}\right)_v = 0$ in the cases that there can be no contact with the line $\left(\frac{dp}{dv}\right)_x$, or only on the side of the liquid volumes. We saw already above, that then the locus of the points of intersection of the two curves mentioned (cf. 7) runs to greater volumes, if x is made to increase. Then at given T , only that part of the line $\left(\frac{dp}{dx}\right)_v = 0$ exists, for which this line runs to greater volume. The lefthand part, for which this curve may reach infinitely large volume lies in the common case at a value of x

to be calculated from $MRT \frac{db}{dx} = \frac{da}{dx}$. Then $\frac{v-b}{v} = \sqrt{\frac{MRT \frac{db}{dx}}{\frac{da}{dx}}}$

and the first part of this equation is then equal to the unity, because $\frac{v}{b} = \infty$. But $\frac{v-b}{v}$ can also be equal to 1 in another case, viz.: if b should be $= 0$. This can only occur, when extrapolating we also admit negative values of x , and moreover choose for b such a function of x that it can become equal to 0 for negative value of x . This is the case for a linear function, but putting $b = b_1(1-x) + b_2x$ is only an approximation. Whether this can also be the case with a more exact shape of $b = f(x)$, must be left undecided. Moreover it is necessary, if we choose always greater negative value of x , that we first find $b = 0$, before finding $\frac{da}{dx} = 0$. But then the shape of the p -lines must also be modified. I shall however not enter into a discussion of this, for one reason because Dr. KOHNSTAMM informed me, that he had already been engaged in the study of the modified course of the isobars, and that he had also come to the conclusion that the relative situation of the values of x , for which $b = 0$ and $\frac{da}{dx} = 0$, is decisive. Moreover I leave undecided for the present whether also on other suppositions than $0 < x < 1$ there can be question of minimum plaitpoint temperature, which is to be distinguished from minimum value of $\frac{a_x}{b_x}$.

Botany. — “*Contribution N^o. 1 to the knowledge of the Flora of Java.*” (Fourth continuation).¹⁾ By Dr. S. H. KOORDERS.

§ 7. *Plantae Junghuhnianae ineditae*. I. Notes on some javanese species of an as yet unpublished collection of Junghuhn's plants, in 's Rijks Herbarium at Leiden.

A few months ago, while searching in 's Rijks Herbarium at Leiden for some herbariumspecimens of JUNGHUHN's Javanese alpine plants, which were required by me, one of the officials of that institution found among the separately preserved collections of “*Indeterminata*” a fairly extensive collection made by JUNGHUHN. This collection had already undergone preliminary determination by me, in 1896 (during a short stay at Leiden), at the request of Dr. J. VALCKENIER SURINGAR, but for the rest remained wholly undetermined.

As I noticed in this collection a number of Javanese alpine plants, and as it seemed worth while to study the collection as a whole, I resolved to complete the determination, begun in 1896, and to publish the results. The latter, as far as an enumeration of the Javanese specimens is concerned, are ready for the press, but will be published separately; here I only append a few remarks on this collection of Junghuhn.

The whole collection consisted of fifteen large packets and fully 560 collecting numbers.

As is the case of very many old herbariumcollections, the labelling of a large number of these specimens left much to be desired. On the other hand some specimens were provided with detailed collecting labels, written by JUNGHUHN himself. With a few exceptions, all the specimens were quite undetermined (without determination of the genus and order). Most of the specimens were also without a collecting number on the label. In consultation with Dr. J. C. GOETHART, Keeper of 's Rijks Herbarium, it was accordingly decided to give running numbers to this whole collection of “*Plantae Junghuhnianae ineditae*”, these numbers being independent of the old numbers, extant in some cases, but not explained by any list or publication. Printed labels have also been added, running partly as follows: “*Plantae Junghuhnianae ineditae. In insula Java legit Dr. FR. JUNGHUHN anno 1838—1863 sub n....*” Except for the substitution of the word “Sumatra” for “Java”, the specimens from Sumatra in this collection have received a similar label.

¹⁾ Continued from these Proceedings p. 132.

I have not been able to ascertain, why this extensive collection of JUNGHUHN'S plants has not been worked at during so many decades, and apparently was never in the hands of MIQUEL. I surmise, in the first place, that it was not received from JUNGHUHN either until the period 1855—1864, or until after his death, *i.e.* after 1864; the receipt of the collection is noted on the outside in an unknown handwriting as "from Bandong". In the second place I surmise that this unpublished collection was accidentally mislaid among the mass of material in 's Rijks Herbarium at Leiden, and was consequently not found again, when MIQUEL was Director of that Institution (1862—1871).

For had this collection been in the hands of one, with so good a knowledge of the East Indian flora as that possessed by MIQUEL, there can, in my opinion, be no doubt, that he would at once have discovered the 9 species mentioned below, which at the time were new to the flora of Java and were found by me undetermined in 1896. Nor would these 9 species have been omitted from the Javanese flora in the publication¹⁾ "*Plantae Junghuhnianae*" of 1854 or in the other publications of MIQUEL (e. g. *Flora Ind. Bat., Ann. Mus. bot. Lugd. Bat., etc.*).

As such I mention the following species:

Pl. Jungh. inedit. n. 368, 380, 381, 385 and 394 = *Turpinia parva* KOORD. et VALETON (first published in 1903) Pl. Jungh. inedit. n. 545 = *Ilex Hookeri* KING (has not yet been mentioned in the literature as occurring in Java), *Itea macrophylla* Wall. var. *minor* K. et V. (at the time not recorded in Java); Pl. Jungh. inedit. n. 207 = *Aglaia heptandra* KOORD. et VALETON (first published in 1896);

¹⁾ The title of this publication is: *Plantae Junghuhnianae. Enumeratio plantarum quas in insulis Java et Sumatra detexit* FR. JUNGHUHN, Leiden, 1854. In the Index Kewensis it is often quoted as MIQUEL Pl. Jungh., although MIQUEL'S name does not appear in the title. Most of the phanerogams in this publication were treated of by MIQUEL himself, some other families by others *i.a.* by BENTHAM (*Leguminosae*), MOLKENBOER (*Loranthaceae*), W. H. DE VRIESE (*Primulaceae*, *Dipterocarpaceae*, etc.), HASSKARL (*Commelynaceae*, *Amaranthaceae*), BÜSE (*Graminae*), BURGERSDIJK (*Violaceae*), and A. J. DE BRUYN (*Polygonaceae*).

In the catalogue of the University library at Leiden, this publication *Plantae Jungh. Enumeratio plant. etc.* (1854) is stated to have appeared in 1851—1855.

In the only copy in 's Rijks Herbarium I found the year 1854 given as the date of publication. This bound copy ends with p. 552, where as the copy of the Royal Academy of Sciences at Amsterdam is slightly more complete, ending with p. 570. The publication seems to have been stopped prematurely, the less incomplete copy of the Royal Academy of Sciences ends on p. 570 *in the middle of a word* and is therefore, evidently no more rounded off than the copy I found at Leiden. The date of publication is given on the title page of the latter copy as 1853.

Pl. Jungh. ined. n. 91 et 103 = *Mallotus campanulatus* J. J. SMITH (first published in 1907 in *Icones Bogoriensis*); Pl. Jungh. ined. n. 113 = *Ostodes macrophylla* BENTH. et HOOK (not recorded for Java even at the present time); Pl. Jungh. ined. n. 462 = *Elaeocarpus Griffithii* A. GRAY (not known for Java at that time); Pl. Jghn. ined. n. 438 = *Saurauja dasyantha* DE VRIESE (even now not mentioned for Java in the literature); Pl. Jghn. ined. n. 256 = *Eugenia cuprea* KOORD. et VALETON published in 1900); Pl. Jghn. ined. n. 426 = *Symplocos Junghuhnii* (published for the first time below).

The specific description is as follows:

Symplocos Junghuhnii KOORD., nova spec. — Arbor ramulis glabris. Folia tenuiter coriacea, supra glaberrima, subtus praeter costam laxe appresse pilosam glabra; 12—15 cm. longa et 4—5 cm. lata, subintegra v. valde indistincte serrulata, basi angustata, apice sensim vel abrupte acute acuminata; nervis secundariis plerumque impressis, petiolo 1—1½, cm. longo. Racemi simplices axillares et terminales villosi petiolo 4—5-plo longiores; bractee ovato-acutae extus basi puberulae calycem aequantes; pedicelli calyce paullo breviores, calycis tubus extus villosus, lobi rotundati glabri marginibus ciliatis, corolla calyce duplo longior utrinque glabra stamina ultra 100 satis distincte pentadelpa; filamenta filiformia glaberrima; ovarium 3-loculare glabrum, stylus glaber; fructus ignotus.

West-Java (Preanger). — Pl. Jungh. ined. n. 426 in Herb. I. B.

The foliage of this species greatly resembles that of *Syml. Henschelii* BRAND [in Engler Monogr. Symploc. Pflanzenw. IV. 242. (1901) 89], but the floral structure is different, as is evident from the above diagnosis.

In the system of the Symplocaceae of BRAND l.c. this species will have to be placed in the subgenus *Hopea* (L. f.) CLARKE, and in the section *Bobua* (DC.) BRAND., and probably in the subsection *Palura* (Buch.-Hamilt.) BENT, et HOOK., immediately near to *Symplocos ribes* JUNGH. et DE VRIESE [in DE VRIESE, Pl. nov. Ind. bat. (1845) 11; BRAND l.c. 39.] Through the extra-ordinarily large number (100) of stamens *Symplocos Junghuhnii* seems to me to differ from *S. ribes*, and from the other more or less closely related Javanese species, *S. aluminosa* BLUME BRAND l.c., *S. odoratissima* (BL.) CHOISY and *S. sessilifolia* (BL.) GÜRKE.

S. polyandra, BRAND. l. c. 36 of the Philippines, which is also related and also has about 100 stamens, is distinguished from the Javanese plant since it has panicles instead of simple racemes.

In 1856 MIQUEL evidently resolved to bring out a second part of the publication, which appeared in 1854 (*Plantae Jungh. Enum. pl.*). This follows for instance from his quoting in the *Flora Ind. Bat. II* (1856) p. 1053: "Pl. Jungh. I. p. 84". My publication on the *Pl. Jungh. ined.* might therefore perhaps have been called "Pl. Jungh. II". Since, however the only part, which appeared in 1854, was not specially designated as part N^o. I, I have now, for the sake of clearness, not called my present publication also "*Plantae Jungh.*", but "*Plantae Junghuhnianae ineditae*".

I found this latter designation for the first time in MIQUEL *Fl. Ind. Bat. I. 2.* (1859) p. 356. An authentic herbariumspecimen of *Flueggea serrata* MIQ., collected by JUNGHUHN in the higher mountain regions of Java, and found by me in the University Herbarium at Utrecht, is published there for the first time and is quoted by MIQUEL l. c. as *Pl. Jungh. inedit.*

The authentic herbarium-labels, preserved at Leiden, which refer to the species treated of in the above-mentioned publication (*Pl. Jungh. Enum. pl.*, 1854) bear numbers, which correspond with that publication of 1854 and are sometimes also quoted in the later publications as *Pl. Jungh. n. 1, 2, 3, etc.* In order to avoid any possible confusion with these numbers, I have quoted below the specimens in the collection now described by me, as follows: *Pl. Jungh. ined. n. 1, 2, etc.*

The number of exclusively alpine Javanese species met with in the above collection, is not large. Nevertheless I found several more or less characteristic Javanese alpine species represented, sometimes by a profusion of specimens. As such the following may be mentioned among others: *Urtica grandidentata* MIQ., *Thalictrum javanicum* BL., *Myrica javanica* BL., *Euphorbia Rothiana* SPRENG., *Viola serpens* WALL., *Leptospermum javanicum* BL., *Clethra canescens* REINW., *Leucopogon javanicus* (JUNGH.) DE VRIESE, *Lysimachia ramosa* WALL. var. *typica* KNUTH., *Primula imperialis* JUNGH., *Buddleia asiatica* LOUR., *Vaccinium Teijsmanni* MIQ., *Vaccinium varingaefolium* MIQ., *Rhododendron retusum* BENN., *Lonicera oxylepis* MIQ., etc.

With some specimens of the collection, now described by me, I found labels, on which, presumably about half a century ago, was written in the hand-writing of the late Professor W. H. DE VRIESE: "*legit Junghuhn, herb. de Vriese*". It seems therefore, that before 's Rijks Herbarium at Leiden acquired this collection of Junghuhn whether by purchase or by donation, it belonged wholly or partly to that herbarium.

The determination of the above-mentioned JUNGHUHN's collection,

was chiefly carried out by me at Leiden, with the aid of the material for comparison in 's Rijk's Herbarium, and for a few rare species with the help of the collections of the University Herbarium at Utrecht.

Leiden, Juni 23rd 1908.

Chemistry. — "*The dynamic conception of a reversible chemical reaction.*" By Prof. A. SMITS and J. P. WIBAUT. (Communicated by Prof. A. F. HOLLEMAN.)

It is generally known that our kinetic views lead to the assumption, that with every reversible reaction we meet with two reactions, which proceed in opposite directions.

The following consideration, however, seemed to show that a direct proof for this dynamic conception could not be given.

Our power of observation only enables us to observe differences; so if we observe something of a conversion, this is the consequence of this that the velocity of one reaction is greater than that of another, and we get an impression as if only one reaction takes place, which proceeds with a velocity equal to the difference of the velocities of the two reactions.

As we shall see, this reasoning, which is perfectly correct for conversions in *homogeneous* systems, does, however, not hold good in all respects in a single case for a conversion in a *heterogeneous* system in consequence of particular circumstances.

The above arguments, however, seemed so convincing that up to now the following *indirect* proof has been considered the only one possible.

The already indicated conception of a reversible reaction leads to a simple relation between the constants of equilibrium and the two constants of reaction, which runs: $K = \frac{k_1}{k_2}$. This relation, now, supplied a means to test the kinetic conception of a reversible conversion, and it is known that experiment has shown for the few cases which have as yet been investigated, that this relation is really satisfied.

Yet it seemed very desirable to prove the correctness of our dynamic conception of a reversible reaction by a *direct* way.

The conversion by means of which we have reached our purpose is this



That the choice fell on this reaction was due to this that it has appeared from the investigations of BOUDOUARD¹⁾ and others that when CO is converted into CO₂ and C, the carbon is deposited in the form of graphite, so that it was to be expected that when we start from the righthand system, and lead CO₂ over *diamond* at constantly increasing temperature, graphite, which will be immediately visible even in exceedingly small quantities will deposit on the diamond, the reaction proceeding simultaneously from left to right.

[It is hardly necessary to observe here that we discuss the reaction in the gas phase, in which the gaseous carbon is one of the reacting components.

The circumstance that the system is heterogeneous, and according to the molecular theoretical views by the side of the homogeneous reaction two more heterogeneous transformations take place, viz.:

diamond \rightarrow C_{vapour} and C_{vapour} \rightarrow graphite, between which the homogeneous reaction forms the link, made us suppose, we had found in this example a means to test our dynamic conception concerning a chemical reaction]²⁾.

It is self-evident that if the experiment is to prove anything, care must be taken that the temperature never falls, because in this case the depositing of graphite might be ascribed to a shifting of the equilibrium from left to right.

To be sure that this was out of the question it was desirable to make the temperature constantly increase during the experiment.

Before proceeding to the experiment we gladly avail ourselves of this opportunity to mention that the diamond powder with which the above mentioned investigation was made, had been kindly supplied to us by Messrs. ASSCHER, to whom we here express our great indebtedness.

As it was important for our investigation to start from white diamond powder, the diamond received by us, which had a grey colour in consequence of impurities, was heated in an open china mug, by means of which a perfectly white powder was obtained.

Before now proceeding to the decisive experiment, it was necessary to investigate first of all whether at the temperature at which we intended to perform our investigation, diamond is already converted to graphite.

For this purpose the white diamond powder was heated for an

¹⁾ Ann. Chim. Phys. (7) 24, 5—85 (1901).

²⁾ The passage between [] is added in the English translation.

hour to 900° in an atmosphere of pure nitrogen by means of an electrical furnace, on which it appeared that under these circumstances nothing was to be detected of a conversion of diamond into graphite.

When this favourable result had been obtained, a china dish filled with diamond powder was placed in a china tube which was slowly heated in an electrical furnace, a current of pure CO₂ passing through the china tube.

The escaping gas was led through a very sensitive solution of PdCl₂, so that the presence of CO in it was at once to be detected.

The experiment showed that under these circumstances the reduction of CO₂ by diamond begins to be noticeable only at about 750°, and proceeds rapidly at 850°.

So after the conversion



had been shown in this way, we had to ascertain whether the reverse reaction



had taken place in the course of this process.

For this purpose the CO₂ stream was suddenly broken while the temperature was still increasing, and the gas-mixture in the china tube was expelled rapidly and completely by means of pure nitrogen. Only then the temperature was lowered, and the furnace cooled down to the temperature of the room.

The contents of the boat showed in an unmistakable way that the latter reaction had really taken place, for the colour had become grayish, in consequence of the depositing of graphite, which had taken place throughout the mass.

On repetition of the experiment the same result was obtained, so that we think that we have given in this way for the first time a *direct* proof of the correctness of the *dynamic* conception of a reversible reaction.

Amsterdam, June 1908.

Anorg. chem. Laboratorium
of the University.

Physics. — “*The P-T-X-spacial figure for a system of two components which are miscible in the solid or liquid crystalline state in all proportions.*” By Prof. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

When we project the spacial figure mentioned in the title above it appears that its most remarkable feature is this that three two sheet surfaces must intersect viz. the vapour-liquid sheet, the vapour-mixed-crystal sheet, and the liquid-mixed-crystal sheet, of which we know that for the simplest case, i.e. for the case that these sheets possess neither maximum nor minimum, they show great resemblance in form.

To examine how this intersection takes place we consider first of all a p - x -figure for a temperature below the triplepoint temperature of the two components.

If we call as is usual, the component with the highest vapour tension (and the lowest triple-point temperature) A , this p - x -diagram has a shape as indicated in fig. 1.

On line acb we find the mixed-crystal phases, which coexist with the vapour phases, which lie on the line adb .

Between these two curves lies the region for vapour + mixed-crystal, $G + F$, and above the line acb the region for the mixed-crystals F , and under adb the region of the vapour G . If now we choose a temperature above the triple-point temperature of A , but below that of B , and if we assume for a moment that at the temperature considered A is found in a solid, so supersolidified state, we get a p - x -figure as indicated by $afbga$ in fig. 2, which is quite analogous to that represented in fig. 1.

Solid A , however, being metastable at this temperature, part of this p - x -figure will be metastable on the A -side, and now the question rises what stable equilibria will take the place of these metastable equilibria.

This is immediately seen when we imagine the case, that the two components are liquid at the temperature considered, and so B occurs in superliquefied state.

In this case we should find a p - x -figure as indicated by $clldgc$, where we notice that d lies below b , and c above a , b and c denoting the vapour tension of metastable states of A and B .

The line $clld$ indicates here the liquid phases coexisting with vapour phases on cgg .

The p - x -figure $afbga$ being metastable on the side of A and $clldgc$ being metastable on the side of B , it is at once evident that

the stable p - x -figure will contain the lefthand part of the former and the righthand part of the latter p - x -figure, which parts will meet where a vapour phase coexists at the same time with a liquid phase and with a mixed-crystal phase.

As follows from the diagram the vapour branches of the two p - x -figures intersect in g , so that g is a vapour which does not only coexist with the liquid l , but also with the mixed-crystal phase f .

So the three-phase-equilibrium $G + L + F$, which is non-variant at constant temperature constitutes the transition between the series of mixed-crystal phases af , and the series of liquid phases ld , which can coexist at a series of pressures with vapour phases of different concentration.

We find the region of the liquid L above the line dl and the region of the mixed crystals F above the line af . The two regions are separated by a region of liquid + mixed crystals lying between the lines lq and fq .

If we now draw some p - x -figures corresponding with different temperatures in the same graphical representation beginning with the triple point temperature of A , and ending with the triple-point temperature of B , we get what is represented in fig. 3.

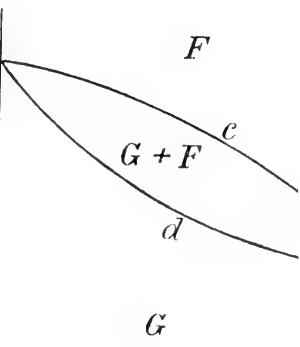
Figure ab corresponds to the triple point temperature of A and a_3b_3 to that of B , the p - x -figures a_1b_1 and a_2b_2 , referring to intermediate temperatures.

From this collection of p - x -figures we see that when we join the corresponding points of the different three-phase-pressure lines glf , a three-phase-region is formed composed of two two-phase-regions, first of the two-phase-region for the equilibria between vapour and liquid, and secondly of a two-phase-region for the coexistence of liquid and mixed crystals.

If we think the p - x -diagrams corresponding with the different temperatures placed in succession, the vapour-lines form a vapour-sheet, the liquid-lines a liquid-sheet, and the mixed-crystal-lines a mixed-crystal-sheet.

The line bgg_1a_3 indicates the intersection of the vapour-sheet of the mixed-crystals¹⁾ with the vapour-sheet of the liquid phases, the line bll_1a_3 that of the liquid sheet of the mixed-crystals with the liquid sheet of the vapour phases, and bff_1a_3 the line along which the mixed-crystal sheet of the liquid phases intersects the mixed-crystal sheet of the vapour phases.

¹⁾ By the vapour sheet of the mixed crystals we must understand here the vapour sheet coexisting with the mixed-crystal sheet.



\mathcal{X}
Fig. 1.

Royal Acad.

All this becomes perfectly clear when we consider the spacial representation, fig. 4, to the *right* of the plane $v_1 v_2 v_3 v_4$.

S_A is the triplepoint of the component A

S_B „ „ „ „ „ „ „ B

cS_A is the vapour-pressure-line of solid A

$S_A K_A$ „ „ „ „ „ „ „ liquid A terminating in the critical point K_A .

aS_B is the vapour-pressure-line of solid B and

$S_B K_B$ „ „ „ „ „ „ „ liquid B terminating in the critical point K_B .

$S_A S'_A$ is the melting-point-line of A and $S_B S'_B$ the melting-point-line of B .

$S_A g S_B f S_A$ is the three-phase-region discussed before, and the v, x -section drawn between the triple-points S_A and S_B shows that $S_A g S_B$ is the vapour line, $S_A l S_B$ the liquid line, and $S_A f S_B$ the mixed-crystal line.

On the two-phase-region $S_A g S_B l S_A$ lie the vapour and liquid phases which are in equilibrium with the mixed-crystals, and on the two-phase-region $S_A l S_B f S_A$ are found the liquid and the mixed-crystal phases which can coexist with the vapour.

The two-sheet surface for mixed-crystal and liquid rests on this latter two-phase-region, which surface will in general be very steep. It has been assumed in the spacial figure that as is actually the case as a rule, $\frac{dp}{dt}$ of the melting-point lines of the components is at first positive, which causes the two-sheet surface mentioned to run to higher temperatures with increasing pressure, which is here represented in an exaggerated manner.

A consequence of this situation is this that, as has been indicated in the section, at a temperature lying between the triple-point temperatures of A and B , the region for liquid and mixed crystal ceases to exist above a certain pressure, r , so that the three regions of two-phase equilibria, mixed-crystal-vapour, liquid-vapour, and mixed-crystal-liquid are limited on all sides.

It is evident that when $\frac{dp}{dt}$ is negative for both melting-point lines, point r will not lie on the melting-point line of the component A , but on that of B .

In the case that the two components pass into the fluid-crystalline state before melting, the spacial figure of such a system is represented by the whole of figure 4 for the simplest case.

The lefthand part agrees then perfectly with BAKHUIS ROOZEBOOM's spacial figure, O_A and O_B not representing the melting-points under vapour-pressure, but the transition points of the two components under vapour pressure, i. e. the points where the ordinary crystalline state passes to the fluid crystalline state under the pressure of its vapour.

If this spacial figure is cut by a plane of constant pressure, we get, at least if this pressure is chosen high enough, the simplest imaginable T - X -figure of a system of two components, each of which possesses a stable fluid-crystalline modification.

The other possible cases may be easily derived from this spacial figure.

Amsterdam June 1908.

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Physics. — “*The liquefaction of helium*”. By Prof. H. KAMERLINGH ONNES. Communication N°. 108 from the Physical Laboratory at Leiden.

§ 1. *Method.* As a first step on the road towards the liquefaction of helium the theory of VAN DER WAALS indicated the determination of its isotherms, particularly for the temperatures which are to be attained by means of liquid hydrogen. From the isotherms the critical quantities may be calculated, as VAN DER WAALS did in his Dissertation among others for the permanent gases of FARADAY, which had not yet been made liquid then, either by first determining a and b , or by applying the law of the corresponding states. Led by the considerations of Comm. N°. 23 (Jan. 1896)¹⁾ and by the aid of the critical quantities the conditions for the liquefaction of the examined gas may be found by starting from another gas with the same number of atoms in the molecule, which has been made liquid in a certain apparatus. By a corresponding process in an apparatus of the same form and of corresponding dimensions the examined gas may be made liquid.

¹⁾ [Developed in view of the statical liquefaction of hydrogen and the obtaining of a permanent bath of liquid hydrogen (Comm. N°. 94*f*) at which I was working then].

By [] will be designed additions made in the translation.

The JOULE-KELVIN effect, which plays such an important part in the liquefaction of gases whose critical temperature lies below the lowest temperature down to which we can permanently cool down, may be calculated from the isotherms, at least if the specific heat in the gas state is not unknown, and its determination, though more lengthy than that of the isotherms, may be an important test of our measurements. If there is to be question of statical liquefaction of the gas by means of the JOULE-KELVIN effect, this must at all events give a decrease of temperature at the lowest temperature already reached, which, as was demonstrated in the above communication, will be the case to a corresponding amount for gases with the same number of atoms¹⁾ in the molecule at corresponding states, while a mon-atomic gas compared with a di-atomic one will be in more favourable circumstances for liquefaction (Comp. also Comm. N^o. 66, 1900).

But the sign of the JOULE-KELVIN effect under certain circumstances does not decide the question whether an experiment on the statical liquefaction of a gas will succeed. Speaking *theoretically*, when by the JOULE-KELVIN effect, at a certain temperature a decrease of temperature however slight can be effected, liquid may be obtained by an adiabatic process with a regenerator coil and expansion cock with preliminary cooling down of the gas to that temperature. But as long as we remain too near the point of inversion the JOULE-KELVIN effect will have a slight value; accordingly the processes by which really gas was liquefied in statical state with an apparatus of this kind, as those which were applied to air by LINDE and HAMPSON, and to hydrogen by DEWAR, start from a much lower reduced temperature, viz. from about half the reduced temperature at which the sign of the JOULE-KELVIN effect at small densities is reversed, or more accurately from somewhat below the BOYLE-point, i.e. that temperature at which the minimum of pv is found at very small densities. [Experiments from which could be derived at how much higher reduced temperature the process still succeeds with mon-atomic gases are lacking]. So according to the above theorem it is *practically* the question whether the lowest temperature at our disposal lies below this BOYLE-point²⁾

¹⁾ [The inversion points of the effect having reference to the amount 0 and therefore being independent of the number of atoms in the molecule, are at corresponding states, and the inversion point for small densities is at corresponding temperature for *all* gases as far as they obey the law of corresponding states. This is easily deduced from the considerations of Comm. N^o. 23].

²⁾ [The BOYLE point, as well as the JOULE-KELVIN inversion point for small densities is a corresponding temperature and both temperatures are therefore proportional theoretically. In the present question it is better to refer to the BOYLE point than to the JOULE-KELVIN inversion point considering the deviations of the law of corresponding states].

which is to be calculated from the isotherms, and the JOULE-KELVIN effect has therefore a sufficient value to yield an appreciable quantity of liquid in a given apparatus in a definite time.

Three years ago I had so far advanced with the investigations which led to the isotherms of helium,¹⁾ that these determinations themselves could be taken up with a reasonable chance of success.

At first the great difficulty was how to obtain sufficient quantities of this gas. Fortunately the Office of Commercial Intelligence at Amsterdam under the direction of my brother, Mr. O. KAMERLINGH ONNES, to whom I here express my thanks, succeeded in finding in the monazite sand the most suitable commercial article as material for the preparation, and in affording me an opportunity to procure large quantities on favourable terms. The monazite sand being inexpensive, the preparation of pure helium in large quantities became chiefly a matter of perseverance and care.²⁾

The determination of isotherms of helium was not accomplished before 1907.

The results of the determinations of the isotherms were very surprising. They rendered it very probable that the JOULE-KELVIN effect might not only give a decided cooling at the melting point of hydrogen, but that this would even be considerable enough to make a LINDE-HAMPSON process succeed.

Before the determinations of the isotherms had been performed I had held a perfectly different opinion in consequence of the failure of OLZEWSKI's and DEWAR's attempts to make helium liquid, and had even seriously considered the possibility that the critical temperature of helium, might lie if not at the absolute zero-point, yet exceedingly low. In order to obtain also in this case the lower temperatures, which among others are necessary for continuing the determinations of isotherms below the temperatures obtainable with solid hydrogen, I had e.g. been engaged in designing a helium motor (cf. Comm. N^o. 23) in which a vacuumglass was to move to and fro as a piston in another as a cylindre. And when compressed helium was observed to sink in liquid hydrogen (Comm. N^o. 96, Nov. 1906) I have again easily suffered myself to be led astray to the erroneous supposition of a very low critical temperature.

In the meantime I had remained convinced that only the deter-

¹⁾ [Comp. for cryostats: Comm. Ns. 14, 51, 83, 94, for thermometry: Comm. Ns. 27, 60, 77, 93, 95, 99, 101, 102, for manometers, piezometers and determination of isotherms: Comm. Ns. 44, 50, 69, 70, 71, 78, 97, 99, 100].

²⁾ [Even the quantity of 200 liters (and 160 liters of reserve) of the extreme purity required, though requiring a great deal of labour, was not out of reach].

mination of the isotherms could decide how helium could be made liquid. Hence we had proceeded with what might conduce to making a favourable result for the critical temperature at once serviceable. Thus the preparation of a regenerator coil with expansion cock in vacuum glass (to be used at all events below the point of inversion), and the preparation of pure helium was continued. Of the latter a quantity had even been gradually collected sufficiently large to render a determination of the JOULE-KELVIN effect in an apparatus already put to the test in preliminary investigations possible, and to enable us to make efficient expansion experiments.

All at once all these preparations proved of the greatest importance when last year (Comm. N°. 102*a*) the isotherms began to indicate 5° K to 6° K for the critical temperature, an amount which according to later calculations, which will be treated in a subsequent paper, might have been put slightly higher (e. g. $0,5'$), and which was in harmony with the considerable increase of the absorption of helium by charcoal at hydrogen temperatures, on the strength of which DEWAR had estimated the critical temperature of helium at 8° K. For according to the above theorem it was no longer to be considered as impossible to make helium liquid by means of a regenerator coil, though this was at variance with the last experiments of OLSZEWSKI, who put the critical temperature below 2° .

It is true that the conclusions drawn from the isotherms left room for doubt. It seemed to me that the isotherms at the lowest temperature yielded a lower critical temperature than followed from the isotherms at the higher temperatures, which is due to peculiarities, which have been afterwards confirmed by the determination of new points on the isotherms. So there was ample room for fear that helium should deviate from the law of the corresponding states, and that still lower isotherms than those already determined should give a still lower critical temperature than 5° K., and according as the critical temperature passed on to lower temperatures the chance to make helium liquid by means of the JOULE-KELVIN effect beginning at the lowest temperatures to be reached with liquid hydrogen (solid hydrogen brings new complications with it) became less. This fear could not be removed by the expansion experiment which I made some months ago, and in which I had thought I perceived a slight liquid mist. (Comm. N°. 105 Postscriptum March 1908). For in the first place only an investigation made expressly for the purpose could decide whether the mist was distinct enough, and whether the traces of hydrogen the presence of which was still to be demonstrated spectroscopically, were slight enough to allow us to attach any im-

portance to the phenomenon. And in the second place the mist was very faint indeed, which might point to a lower critical temperature than had been derived.

So it remained a very exciting question what the critical temperature of helium would be. And in every direction in which after the determination of the isotherms in hand we might try to get more information about it, we were confronted by great difficulties.

As, however, they consisted in the arrangement of a cycle with cooled helium, [this being indispensable to integrate cooling effects with a reasonable quantity of helium] the labour spent for years on the arrangement of the Leiden cascade of cycles for accurate measurements, might contribute to the surmounting of them. Arrived at this point I resolved to make the reaching of the end of the road at once my purpose, and to try and effect the statical liquefaction of helium with a circulation, as much as possible "corresponding" to my hydrogen circulation.

In this I perfectly realized the difficulty to satisfy at the same time the different conditions for success [allowing for possible deviations from the law of corresponding states]. For [though the suitability of the hydrogen cycle for the cooling down of the compressed helium to 15° K. was amply proved (Comm. N^o. 103)] the preliminary cooling to be reached was, as to the temperature, only just within the limit at which it could be efficient, nor were the other circumstances which could be realized, any more favourable.

Of course the scale on which the apparatus intended for the experiment in imitation of the apparatus which had proved effective for hydrogen, would be built, was not only chosen smaller in agreement with the value of b which was put lower, but taken as small as possible. That the reduction of HAMPSON'S coil to smaller dimensions does not diminish its action had been found by former experiments, and has been very clearly proved by what OLSZEWSKI tells about the efficiency of his small hydrogen apparatus. I could not, however, reduce below a certain limit without meeting with construction problems, about which the hydrogen apparatus had not given any information. We had to be sure that the capillaries would not get stopped up, that the cocks would work perfectly, that the conduction of heat, friction etc. would not become troublesome. When in connection with the available material, the smallest scale at which I thought the apparatus still sufficiently trustworthy, reduction to half its size, had been fixed, the dimensions of the regenerator coil, though as small as those of OLSZEWSKI'S coil, proved

still so large that the utmost was demanded of the dimensions of the necessary vacuum glasses; which was of the more importance, because the bursting of the vacuum glasses during the experiment would not only be a most unpleasant incident, but might at the same time annihilate the work of many months.

Besides the difficulties given by the helium liquefactor itself, the further arrangement of the cycle in which it was to be inserted, offered many more.

The gas was to be placed under high pressure by the compressor, and was to be circulated with great rapidity. Every contamination was to be avoided, and the spaces which were to be filled with gas under high pressure were to have such a small capacity, that they only held part of the available naturally restricted quantity of helium.

As compressor only CAILLETET'S modified compressor could be used, a compressor with mercury piston, which had been arranged for experiments with pure and costly gases, and was described in Comm. N^o. 14 (Dec. 1894) and Comm. N^o. 54 (Jan. 1900), and which also served for the compression of the helium in the expansion experiments of last March (Comm. N^o. 105)¹.

That it could only be charged to 100 atms., a fact which I had sometimes considered as a drawback in the case of experiments with helium, could no longer be deemed a drawback after the determinations of isotherms had taught that even if the pressure of helium compressed above 100 atms. at low temperatures is raised much, the density of the gas increases but little. Accordingly I had not gone beyond 100 atms. in my expansion experiments. The higher pressures which DEWAR and OLSZEWSKI applied in their expansion experiments, have been a decided disadvantage, because they involved the use of a narrower expansion tube. With regard to the circulation now to be arranged, with estimation of the critical pressure at 7 or 5 atms.²), according as *b* was put at a third or half that of hydrogen, a pressure of 100 atms. in the regenerator coil had to be considered as sufficient according to the law of corresponding states.

But for a long time it was considered an insuperable difficulty that the compressor conjugated to the auxiliary compressor could circulate at the utmost 1400 liters of gas measured at the ordinary

¹) [Just as when it was used to get a permanent bath of liquid oxygen (completed 1894 Comm. N^o. 14) it was now again in the pioneering cycle and rewarded well the work spent on it, especially in 1888 when I was working at the problem to pour off liquid oxygen in a vessel under atmospheric pressure by the help of the ethylene cycle].

²) [The results of the isotherm of helium at -259° to be treated in a following communication were not yet available then; they point to a smaller value].

temperature per hour, $\frac{1}{15}$ of the displacement with the hydrogen circulation. Not before experiments with the latter had been made, in which the preliminary cooling of the hydrogen did not take place with air evaporating at the vacuum pump (so at -205°) but under ordinary pressure (so at -190°), and moreover the hydrogen compressor ran 4 times more slowly than usual, and in these experiments liquid hydrogen had yet been obtained, it might be assumed that the circulation process to be realized would still be sufficient to accumulate liquid helium.

With regard to the parts of the compressors, the auxiliary apparatus, and the conduits, which in the course of the experiment assume the same pressure as the regenerator coil, their joint capacity was small enough to enable us to make the experiment with a quantity of 200 liters. This quantity of pure helium besides a certain quantity [160 liters] kept in reserve could be ready within not too long a time¹⁾.

A great difficulty of an entirely different nature than the preceding one consisted in this that the hydrogen circulation and the helium circulation could not be worked simultaneously with the available helpers to work them. It is true that the two circulations have been arranged not only for continuous use, but if there is a sufficient number of helpers, also for simultaneous use, but in a first experiment it was out of the question to look, besides after the helium circulation, also after the hydrogen circulation, the working of which requires of course, great experience²⁾. So on the same day that the helium experiment was to be made, a store of hydrogen had to be previously prepared large enough to provide for the required cooling during the course of the helium experiment. It was again the law of corresponding states which directed us in the estimation of the duration of the experiment and the required quantity of liquid hydrogen³⁾. They remained just below the limit at which the arrangement of

¹⁾ [That success was only possible by applying the cycle method is evident from the fact that the helium has passed the valve 20 times before liquefaction was observed, and the considerable labour expended on the preparation of the pure helium would have been increased in the same proportion i.e. to an extravagant amount].

²⁾ [Now the great difficulties of a first liquefaction have been overcome simultaneous working has become possible, though it remains the question how to find the means to develop the laboratory service according to the extension of its field of research].

³⁾ [The hydrogen cycle is not only arranged so that the same pure hydrogen in it can be circulated and liquefied at the rate of 4 liters per hour as long as this is wished, but also allows (as will be treated in a following communication) easily to prepare great stores of extremely pure hydrogen gas, which can be tapped off from the apparatus as liquid at the rate of 4 liters per hour].

the experiment in the designed way would be unadvisable, but how near this limit was has appeared later.

In all these considerations the question remained whether everything that could appear during the experiment, had been sufficiently taken into account in the preparation. So we were very glad when the calculation of the last determined points on the isotherm of -259° shortly before the experiment confirmed that the BOYLE-point [though below the boiling point of hydrogen] lay somewhat above this lowest temperature of preliminary cooling, and at least the foundation of the experiment was correct.

In the execution I have availed myself of different means which DEWAR has taught us to use. I have set forth the great importance of his work in the region of low temperatures in general elsewhere (Comm. Suppl. N^o. 9, Febr. 1904), here, however, I gladly avail myself of the opportunity of pointing out that his ingenious discoveries, the use of silvered vacuum glasses, the liquefaction of hydrogen, the absorption of gases in charcoal at low temperatures, together with the theory of VAN DER WAALS, have had an important share in the liquefaction of helium.

§ 2. *Description of the apparatus.* The whole of the arrangement has been represented on Pl. I. We mentioned before that in virtue of the principles set forth in Comm. N^o. 23 the construction of the helium liquefactor (see Pl. II and III) was as much as possible an imitation of the model of the hydrogen liquefactor described before (Comm. N^o. 94 ϵ , May 1906), to which I therefore refer in the first place.

It was particularly difficult to keep the hydrogen, which evaporating under a pressure of 6 cm. is to cool the compressed helium to 15° K. (just above the melting point of hydrogen), on the right level in the refrigerator intended for this purpose. This difficulty was surmounted in the following way: The liquid hydrogen is not immediately conveyed from the store bottles into the refrigerator, but first into a graduated glass *Ga* in the way indicated before, which on comparison of the figures from Comm. N^o. 94 ϵ and N^o. 103 Pl. I fig. 4 does not require a further explanation. This graduated glass was a non-silvered vacuum glass, standing in a silvered vacuum glass *Gb* with liquid air, in which on either side the silver coating had been removed over a vertical strip so as to enable us to watch the level of the hydrogen in the graduated glass. From this vacuum glass the liquid hydrogen is siphoned over into the hydrogen refrigerator by means of a regulating cock *P*. To see whether the level of the liquid in the refrigerator takes up the right position, the german silver reservoir N_1 of a helium thermometer has been

soldered to the tube which conveys at an initial temperature of -190° the compressed helium which is to be cooled down further. This reservoir leads through a steel capillary N_2 (as in Comm. N^o. 27, May, 1896) to a reservoir N_4 with stem N_3 . The quantity of helium and the pressure have been regulated in such a way that the mercury stands in the top of the stem, when the thermometer reservoir is quite immersed in hydrogen of 15° K, while as soon as the level falls, this is immediately shown by the fall of the mercury. The same purpose is further served by two thermoelements constantan iron (see Comm. N^o. 89 Nov. 1903 and N^o. 95a June 1906) one on the bottom, the other soldered to the spiral on the same level as the thermometer reservoir. They did not indicate the level in the experiment of July 10th, because something got defect.

The evaporated hydrogen contributes in the regenerator D_b to save liquid air during the cooling of the compressed helium, and is sucked up (along 15 and H_c) in the large cylindre of the conjugated methylchloride pump (Comm. N^o. 14 Dec. 1894), which otherwise serves in the methylchloride circulation of the cascade for liquid air; it is further conducted through an oil-trap, and over charcoal to the hydrogen gas-holder (Comm. N^o. 94*f*), from which the hydrogen compressor (Comm. N^o. 94*f*) forces the gas again into the store cylindres.

To fill the helium circulation the pure helium passes from the cylindres R_1 (see Pl. II), in which it is kept, into the gasholder floating on oil (cf. Comm. N^o. 94*f*), which is in connection with the space in which the helium expands when issuing from the cock, a german silver cylindre, in which the upper part of the vacuum glass E_a has been inserted. The gas from the gasholder, and afterwards the cold outflowing helium, which has flowed round the regenerator coil, and of whose low temperature we have availed ourselves in the regenerator D_a to save liquid air when cooling the compressed helium, is sucked up by the auxiliary compressor V , and then received in the compressor with mercury piston Q (Comp. Comm. N^o. 54). This forces it (Pl. II and III) along the conduit:

a. through a tube C_a which at its lower end is cooled down far below the freezing point by means of vapour of liquid air, and at its upper end is kept at the ordinary temperature. Here the helium is perfectly dried.

b. through a tube divided into two parts along two refrigerating tubes (in D_a and D_b), in which it is cooled in the one by the abduced hydrogen, in the other by the abduced helium, after which it unites again.

c. through a tube C_b filled with exhausted charcoal immersed

in liquid air. Here whatever traces of air might have been absorbed during the circulation, remain behind.

d. through a refrigerating tube B_3 , lying in the liquid air, which keeps the cover of the hydrogen space and of the helium space cooled down.

e. through a refrigerating tube B_2 , in which it is cooled by the evaporated liquid hydrogen.

f. through the refrigerating tube B_1 , lying in the liquid hydrogen evaporating under a pressure of 6 cm., here the compressed helium is cooled down to 15° K;

g. and from here in the regenerator coil A , which has been fourfold wound as in HAMPSON'S apparatus for air, and in the hydrogen liquefactor of Comm. 94*f*.

Then it expands through the cock M_1 , if it should allow too much gas to pass, this can escape through a safety tube. When the temperature has descended so low that the liquid helium flows out, the latter collects in the lower part of the vacuum glass Ea , which is transparent up to the level of the cock, and is silvered above it.

The outflowing gaseous helium can be made to circulate again by the compressor of the circulation, or be pressed in the supply cylinders R_2 .

At some distance under the expansion cock M_1 , the german silver reservoir Th_1 of a helium thermometer has been adjusted, it is soldered to a steel capillary Th_2 , which is connected with the manometer reservoir Th_4 with stem Th_3 . If the mercury has been adjusted in such a way that at 15° K its level is at the lower end of the just mentioned stem, the stem has sufficient length to prevent the mercury from overflowing into the capillary with further fall of the temperature.

The circulation is provided with numerous arrangements for different operations (for the compressor comp. Comm. n^o. 54). Worth mentioning is an auxiliary tube Z filled with exhausted charcoal, which is cooled by liquid air when used. After the whole apparatus has been filled with pure gas, the gas is circulated through this side-conduit (along 11 and 8) while the tube Cb of charcoal belonging to the liquefactor, is shut off (by M and 9), to free it from the last traces of air which might have remained in the compressor and the conduits.

It now remains to describe in what way it has been arranged that the liquid helium can be observed. Round the transparent bottom part of the vacuum glass a protection of liquid hydrogen has been applied. The second vacuum glass E_b , which serves this purpose, forms a closed space together with the former E_a , and the construction

has been arranged in such a way that first this space can be exhausted and filled with pure hydrogen gas, which is necessary to keep the liquid hydrogen perfectly clear later on. The liquid hydrogen is again conducted into this space in the way of Comm. N^o. 94^f and 103 Pl. I fig. 4; the evaporated hydrogen escapes at *Hg* to the hydrogen gasholder. The hydrogen glass is surrounded by a vacuum glass *E_c* with liquid air, which in its turn is surrounded by a glass *E_d* with alcohol, heated by circulation.

By these contrivances and the extreme purity of the helium we succeeded in keeping the apparatus perfectly transparent to the end of the experiment, after 5 hours. Protection with liquid hydrogen is necessary to reduce the evaporation of the helium to an insignificant degree notwithstanding that the silver coatings of the vacuum glass have been removed. That it ended in a narrower part, and the helium thermometer reservoir not was placed at the lowest point, was because it was possible that only an exceedingly slight amount of liquid was formed. The vacuum glass was made transparent up to the cock in order to enable us to see any mist that might appear and if on the other hand much liquid was formed, to prevent the lower part from getting entirely filled without our noticing it. The latter has actually been the case for some time, and would not have been so soon perceived, if the walls had been silvered further. But if the glass is not silvered, the conduction of heat towards the helium is much greater, and without protection with liquid hydrogen the helium that was formed, might have immediately evaporated.

In the preparation of the vacuumglasses ¹⁾ Mr. O. KESSELRING, glass-blower of the laboratory, has met the high demands put to him, with untired zeal and devotion, for which I here gladly express my thanks to him.

§ 3. *The helium.* As to the chemical part of the preparation of this gas I was successively assisted by Mr. J. WATERMAN, Mr. J. G. JURLING, Mr. W. MEYER-CLUWEN and Mr. H. FILIPPO Jzn. Chem. Docts., who collaborated with Mr. G. J. FLIM, chief of the technical department of the cryogenic laboratory. To all of them I gladly express my indebtedness for the share each of them has had in the arrangement, the improvement, and the simplification of the operation. More particularly to Mr. FILIPPO for his careful analyses and the effective way, in which the last combustion over CuO with addition of oxygen, and avoidance of renewed contamination by hydrogen was carried out by him.

¹⁾ [There was one of each in reserve before the beginning of the experiment. Only one of the reserves had to be used].

The gas was obtained from the monazite (see § 1) by means of heating, it was exploded with oxygen, cooled with liquid air, and, compressed, led over charcoal at the temperature of liquid air. Then it was burned over CuO. Then it was compressed over charcoal at the temperature of liquid air, after which it was under pressure led over charcoal at the temperature of liquid hydrogen several times till the gas which had been absorbed in the charcoal and then separately collected no longer contained any appreciable admixtures.

This way of preparation (to be treated in a following Comm.) was also applied in Comm. N^o. 105.

§ 4. *The experiment.* After on July 9th the available quantity of liquid air had been increased ¹⁾ to 75 liters, all apparatus examined as to their closures, exhausted, and filled with pure gas, we began the preparation of liquid hydrogen on the 10th of July, 5.45 a.m., 20 liters of which was ready for use in silvered vacuum glasses (cf. Comm. N^o. 94/ Pl. III) at 1.30 p.m. In the meantime the helium apparatus had been exhausted while the tube with charcoal belonging to it was heated, and this tube being shut off, the gas contained in the rest of the helium circulation was freed from the last vestiges of air by conduction over charcoal in liquid air through the side-conduit. The hydrogen circulation of the helium apparatus was connected with the hydrogen gasholder and the air-pump, which had served as methyl chloride pump in the preparation of air the day before, and this whole circulation was exhausted for so far as this had not yet been done, and filled with pure hydrogen. Moreover the space between the vacuum glasses (E_a and E_b) which was to be filled with liquid hydrogen as a protection against access of heat, was exhausted and filled with pure hydrogen, and the thermometers and thermoelements were adjusted.

At 1.30 p.m. the cooling and filling of the glasses which, filled with liquid air, were to protect the glasses which were to be filled with liquid hydrogen, began with such precautions that everything remained clear when they were put in their places. At 2.30 a commencement was made with the cooling of the graduated vacuum glass and of the hydrogen refrigerator of the helium liquefactor by the aid of hydrogen led through a refrigerating tube, which was immersed in liquid air. At 3 o'clock the temperature of the refrigerator had fallen to -180° according to one of the thermo-elements. Then the protecting glass (E_b) was filled with liquid hydrogen, and after

¹⁾ [With the help of the regenerative cascade Comp. Comm. N^o. 94, f. XIII and Supplem. N^o. 18].

some delay in consequence of insignificant disturbances, the filling of the graduated vacuum glass and the hydrogen refrigerator with hydrogen began at 4.20 p.m.

At the same time the helium was conducted in circulation through the liquefactor. The pressure under which the hydrogen evaporated, was gradually decreased to 6 c.m., at which it remained from 5.20 p.m. The level in the refrigerator was continually regulated according to the indication of the thermometer-level-indicator and the reading of the graduated glass, and care was taken to add liquid hydrogen (*Hydr. a, Hydr. b* Pl. II) and liquid air wherever necessary (*a, b, c, d*, Pl. II). In the meantime the pressure of the helium in the coil was slowly increased, and gradually raised from 80 to 100 atms. between 5.35 and 6.35 p.m.

At first the fall of the helium thermometer which indicated the temperature under the expansion cock, was so insignificant, that we feared that it had got defect, which would have been a double disappointment because just before also in the gold-silver thermo-element, which served to indicate the same temperature, some irregularity had occurred. After a long time, however, the at first insignificant fall began to be appreciable, and then to accelerate. Not before at 6.35 an accelerated expansion was applied, on which the pressure in the coil decreased from 95 to 40 atms., the temperature of the thermometer fell below that of the hydrogen. In successive accelerated expansions, especially when the pressure was not too high, a distinct fluctuation of the temperature towards lower values was clearly observed. Thus the thermometer indicated e.g. once roughly 6° K.

In the meantime the last bottle of the store of liquid hydrogen was connected with the apparatus: and still nothing had as yet been observed but some slight waving distortions of images near the cock. The thermometer indicated first even an increase of temperature with accelerated expansion from 100 atms., which was an indication for us to lower the circulation pressure to 75 atms. Nothing was observed in the helium space then either, but the thermometer began to be remarkably constant from this moment with an indication of less than 5° K. When once more accelerated expansion from 100 atms. was tried, the temperature first rose, and returned then to the same constant point.

It was, as prof. SCHREINEMAKERS, who was present at this part of the experiment, observed, as if the thermometer was placed in a liquid. This proved really to be the case. In the construction of the apparatus (see § 2) it had been foreseen that it might fill with

liquid, without our observing the increase of the liquid. And the first time the appearance of the liquid had really escaped our observation. Perhaps the observation of the liquid surface, which is difficult for the first time under any circumstance, had become the more difficult as it had hidden at the thermometer reservoir. However this may be, later on we clearly saw the liquid level get hollow by the blowing of the gas from the valve and rise in consequence of influx of liquid on applying accelerated expansion, which even continued when the pressure descended to 8 atms. So there was no doubt left that the critical pressure lies also above one atmosphere. If it had been below it, the apparatus might all at once have been entirely filled with liquid compressed above the critical pressure, and only with decrease of pressure a meniscus would have appeared somewhere in the liquid layer; this has not taken place now.

The surface of the liquid was soon made clearly visible by reflection of light from below, and that unmistakably because it was clearly pierced by the two wires of the thermoelement.

This was at 7.30 p. m. When the surface had once been seen, it was no more lost sight of. It stood out sharply defined like the edge of a knife against the glass wall. Prof. KUENEN, who arrived at this moment, was at once struck with the fact that the liquid looked as if it was almost at its critical temperature. The peculiar appearance of the helium may really be best compared with that of a meniscus of carbonic acid e. g. in a Cagniard de la Tour-tube. Here, however, the tube was 5 cm. wide. The three liquid levels in the vacuum glasses being visible at the same time, they could easily be compared; the difference of the hydrogen and the helium was very striking.

When the surface of the liquid had fallen so far that 60 cm³. of liquid helium still remained — so considerably more had been drawn off — the gas in the gasholder was exhausted, and then the gas which was formed from this quantity of liquid was again separately collected. In the course of the experiment the purity of this gas was determined by means of a determination of the density (2,01), which was afterwards confirmed by an explosion experiment with oxyhydrogen gas added, and further by a careful spectroscopical investigation.

At 8.30 the liquid was evaporated to about 10 cm³., after which we investigated whether the helium became solid when it evaporated under decreased pressure. This was not the case, not even when the pressure was decreased to 2,3 cm. A sufficient connection could not be

quickly enough established with the large vacuum pump, which exhausts to 2 mm., so this will have to be investigated on another occasion. The deficient connection, however, has certainly made the pressure decrease below 1 cm., and perhaps even lower. That 7 mm. has been reached, is not unlikely.

At 9.40 only a few cm³. of liquid helium were left. Then the work was stopped. Not only had the apparatus been taxed to the uttermost during this experiment and its preparation, but the utmost had also been demanded from my assistants.

But for their perseverance and their ardent devotion every item of the program would never have been attended to with such perfect accuracy as was necessary to render this attack on helium successful.

In particular I wish to express my great indebtedness to Mr. G. J. FLIM, who not only assisted me as chief of the technical department of the cryogenic laboratory in leading the operations, but has also superintended the construction of the apparatus according to my direction, and rendered me the most intelligent help in both respects.

§ 5. *Control experiments.* All the gas that had been used in the experiment, was collected in three separate quantities and compressed in cylinders. Quantity *A* contains what was finally left in the apparatus. Quantity *B* has been formed by evaporation of a certain quantity of liquid helium. Quantity *C* is the remaining part that has been in circulation. Together they yielded the same quantity as we started with. They were all three exploded with addition of oxyhydrogen gas and excess of oxygen; no hydrogen could be demonstrated. For the density (in a single determination) we found ($0 = 16$) $A = 2.04$, $B = 1.99$, $C = 2.02$.

The spectrum of the gas used for the experiment put in a tube with mercury closure without electrodes and freed beforehand from vapour of water and fat at the temperature of liquid air, answered (only the spectrum of the capillary has been investigated) the description given by COLLIE of the spectrum of helium with a trace of hydrogen and mercury vapour.

Spectroscopically both the distilled *C*, and *B* were somewhat purer than the original gas. In the latter the hydrogen lines gained in case of high vacua, in the former the helium disappeared last. The hydrogen, from which the latter has still been cleared, must be found in *A*. By means of absorption by charcoal 8 c.m³. of hydrogen was separated from this. To this would correspond a difference in percentage of hydrogen before and after the experiment of 0.004 %.

To estimate the percentages of hydrogen the spectra of the just-mentioned quantities were compared with the spectrum of a helium which could not contain much more than 0.005 % hydrogen according to an estimation founded on the quantities of hydrogen which had been absorbed from the gas the last few times of successive purification when it was led compressed over charcoal at the temperature of liquid hydrogen, and with the spectrum of this helium after 0,1 % hydrogen had been mixed with it.

The gas used for the experiment did not differ much from that which served for comparison, and of which the red hydrogen and the helium lines vanished simultaneously for the highest vacua, but it seemed to be somewhat less pure, for the red hydrogen line preponderated over the helium line for the highest vacua. In the different spectra the hydrogen line was not to be seen at a pressure of 32 mm., the *F*-line with an intensity of 0,01 of He 5016; at 12–16 mm. *C* was faint compared with He 6677, and *F* faint compared with He 5016. An amount varying between 0,01 and 0,3 was assumed for the ratio of the intensity.

On the other hand at 32 mm. the *C* in the mixture with 0,1 pCt. hydrogen had already the same intensity as He 6677, *F* 0,3 of He 5016, which remained the case at 16 mm. (somewhat less for *C*, somewhat more for *F*).

In spite of the precautions taken it was observed a single time that the hydrogen lines increased in intensity during the determination, so when we proceeded to lower pressures the determinations became unreliable. These comparisons are, therefore, very imperfect; but then, the examination how traces of hydrogen in helium may be quantitatively determined by a spectroscopic method would constitute a separate investigation. In connection with the above difference in content of *B* and *C* with the original gas, the observations mentioned may perhaps serve to show that these percentages have not been much more than 0,004 and 0,008.

The purity of the helium had already been beyond doubt before, for the cock worked without the least disturbance, and no turbidity was observed even in the last remaining 2 cm³. of liquid.

The reliability of the helium thermometer was tested by the determination of the boiling point of oxygen, for which 89° K. was found instead of 90° K. We must however, bear in mind that the thermometer has not been arranged for this temperature and the accuracy in percents of the total value is considerably higher for the much lower temperature of liquid helium.

For the assistance rendered me in the different control experiments, I gladly express my thanks to Dr. W. H. KEESOM and Mr. H. FILIPPO Jzn.

§ 6. *Properties of the helium.* By the side of important points of difference the properties of helium present striking points of resemblance with the image which DEWAR drew in his presidential address in 1902 on the strength of different suppositions.

We mentioned already the exceedingly slight capillarity.

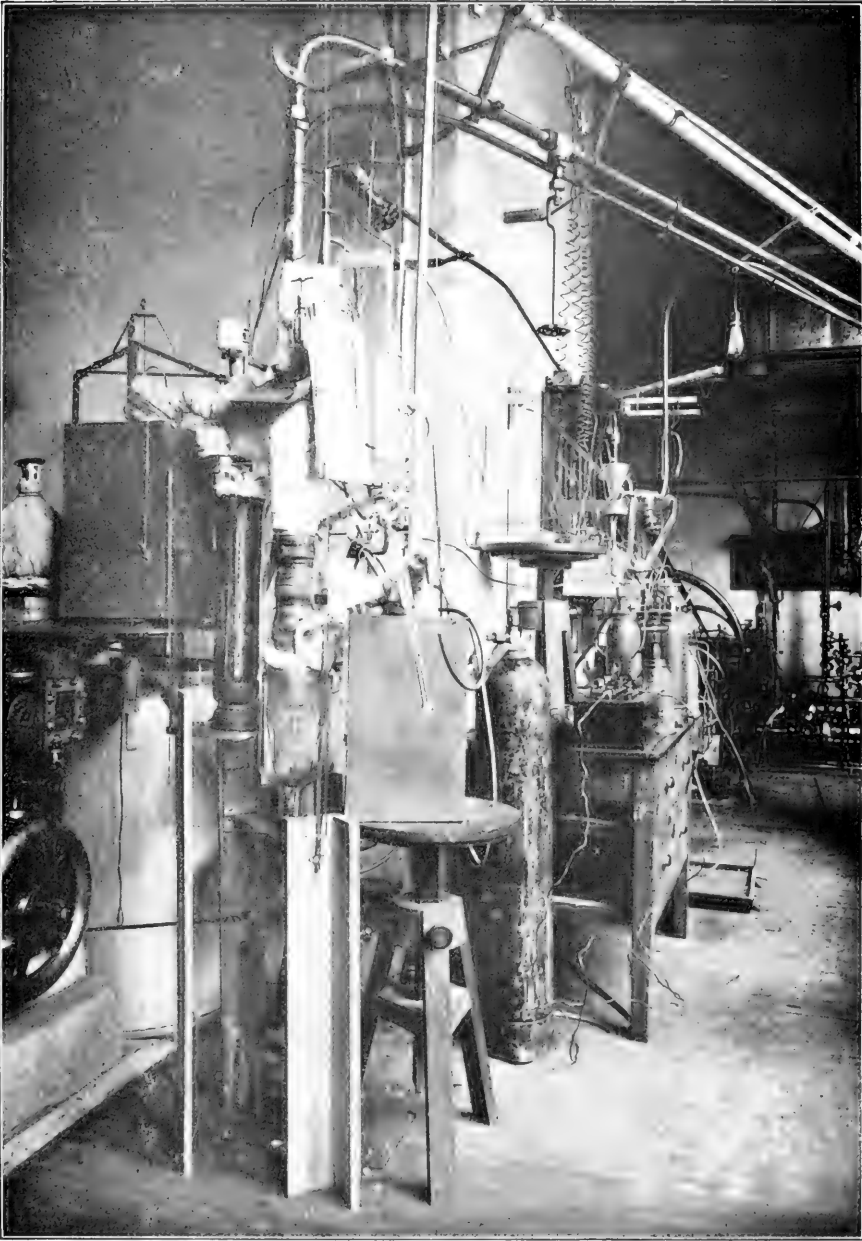
For the boiling-point we found $4^{\circ}.3$ on the helium thermometer of constant volume at 1 atm. pressure at about 20°K . This temperature is still to be corrected to the absolute scale by the aid of the equation of state of helium. The correction may amount to some tenths of degrees if a increases at lower temperatures, so that the boiling-point may perhaps be rounded off to $4^{\circ}.5$ K.

The triple-point pressure if it exists lies undoubtedly below 1 cm., perhaps also below 7 mm. According to the law of corresponding states the temperature can be estimated at about 3°K at this pressure. The viscosity of the liquid is still very slight at this temperature. If the helium should behave like pentane, we could descend to below 1.5°K before it became viscous, and still lower near 1°K before it became solid. How large the region of low temperatures (and high vacua) is that has now been opened, is, however, still to be investigated.

Liquid helium has a very slight density, viz. 0.15. This is smaller than was assumed and gives also a considerably higher value of b than can be derived from the isotherms at $-252^{\circ}.72$ and $-258^{\circ}.82$ now that the points mentioned in § 1 have been determined, viz. about 0.0007 provisionally. The value of b which follows from the liquid state is about double the value of b which was expected [viz. 0,0005], and was assumed in the calculations of Dr. KEESOM and myself on mixtures of helium and hydrogen (Comp. Suppl. N^o. 16 Sept. '07 § 1 fn. 5).

From the high value of b follows immediately a small value of the critical pressure, which probably lies in the neighbourhood of 2 or 3 atms., and is exceedingly low in comparison with that for other substances. So when helium is subjected to the highest pressures possible, the "reduced" pressures become much higher than are to be realized for any other substance. What may be obtained in this respect, by exerting a pressure of 5000 atms. on helium exceeds what would be reached when we could subject carbonic acid e.g. to a pressure of more than 100.000 atms.

The ratio of the density of the vapour and that of the liquid is



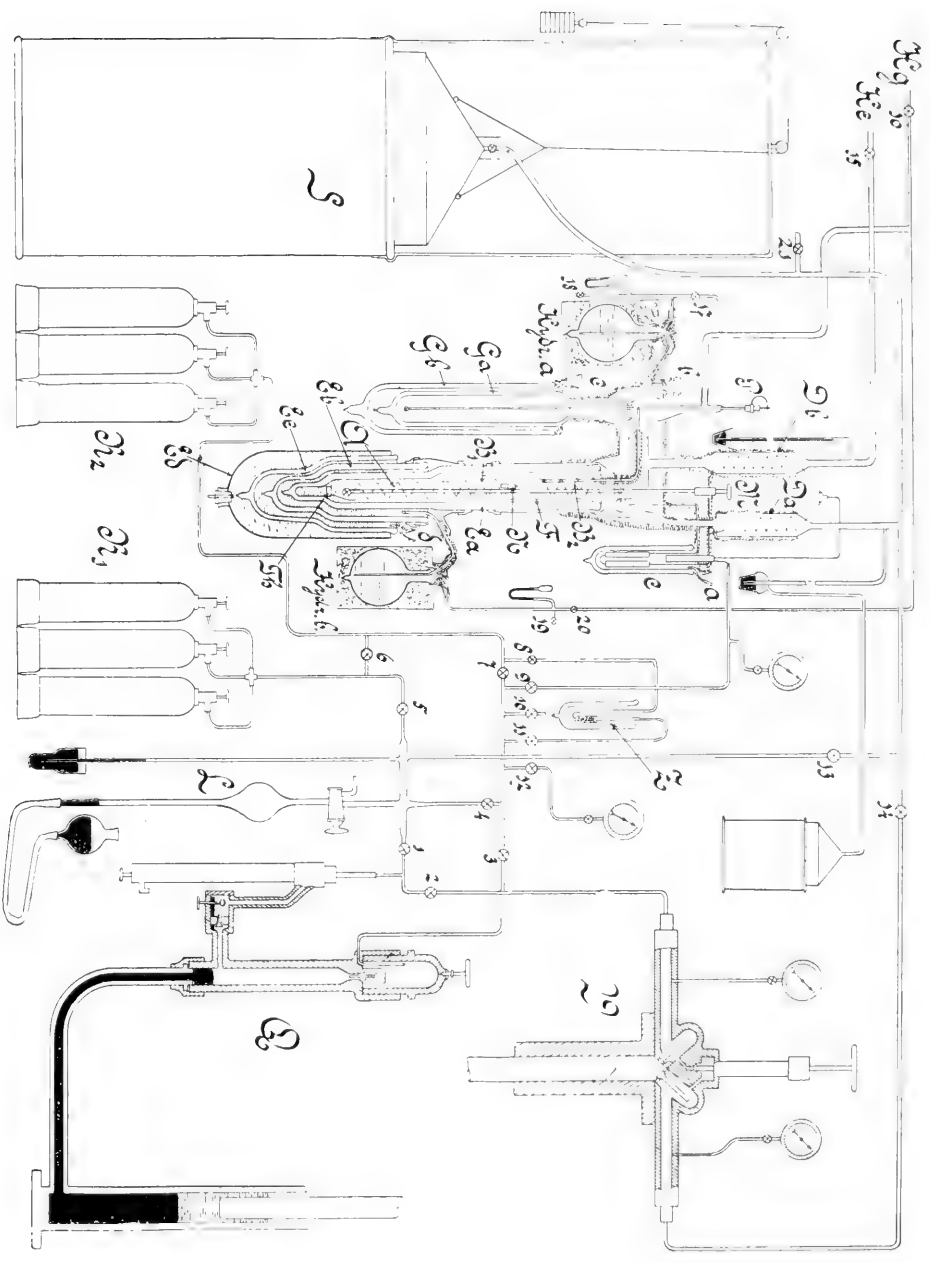


Plate II.

about 1 to 11 at the boiling-point. It points to a critical temperature which is not much higher than 5° K., and a critical pressure which is not much higher than 2,3 atms.

But all the quantities mentioned will have to be subjected to further measurements and calculations before they will be firmly established, and before definite conclusions may be drawn from them.

We may only still mention here a preliminary value of a , viz. 0.00005. When in 1873 VAN DER WAALS in his Dissertation considered whether hydrogen would have an a , it was only after a long deliberation that he arrived at the conclusion that this must exist, even though it should be very small. It may be presumed that matter will always have attraction, was his argument, and as chance would have it these words were repeated by him in reference to helium some days before the liquefaction of helium (These Proc. June 1908). The a found now denotes the smallest degree of this attraction of matter, which still manifests itself with remarkable clearness also in helium in its liquefaction.

Geology. — *“The age of the layers of Sondé and Trinil on Java”.*

By Prof. K. MARTIN.

(This paper will not be published in this Proceedings).

(September 8, 1908).



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETINGS
of Saturday September 26, 1908.

(Translated from: Verslag van de gewone vergaderingen der Wis- en Natuurkundige
Afdeling van Zaterdag 26 September 1908, Dl. XVII).

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Physics. — "*Contribution to the theory of binary mixtures.*" VIII.
 By Prof. J. D. VAN DER WAALS.

THE INTERSECTION OF THE CURVE $\frac{d^2p}{dv dx} = 0$ WITH $\frac{dp}{dv} = 0$.

By the aid of the approximate equation of state the course of the
 curve $\frac{d^2p}{dv dx} = 0$ is given by the equation:

$$\frac{MRT \frac{db}{dx} \frac{da}{dx}}{(v-b)^3} = \frac{1}{v^3}.$$

As has been observed before, it has a course which is analogous
 to that of the curve $\frac{dp}{dx} = 0$. At given value of T it has an asymp-

tote for that value of x , for which in rarefied gas state, the deviation from the law of BOYLE is maximum, viz. for which $MRT \frac{db}{dx} = \frac{da}{dx}$.

It has minimum volume on the line $v - b = 3 \frac{db}{dx} \frac{dx}{d^2a}$, whereas the

line $\frac{dp}{dx} = 0$ has such a minimum volume on the line $v - b = 2 \frac{db}{dx} \frac{dx}{d^2a}$.

The points of intersection of $\frac{d^2p}{dv dx} = 0$ and $\frac{dp}{dx} = 0$ indicate the points in which $\frac{dp}{dv} = 0$ has a tangent parallel to the X -axis, as follows

from $\frac{d^2p}{dv^2} \frac{dv}{dx} + \frac{d^2p}{dx dv} = 0$. For such a point of intersection we have

at the same time $\frac{MRT}{(v-b)^2} = \frac{2a}{v^3}$ and $\frac{MRT \frac{db}{dx} \frac{da}{dx}}{(v-b)^3} = \frac{da}{v^3}$; and so $\frac{db}{v-b} = \frac{da}{2a}$,

which last equation represents the locus of these points of intersection.

Differentiating this locus " $v - b = 2 \frac{db}{dx} \frac{a}{da}$ " we find:

$$\frac{dv}{dx} = \frac{db}{dx} \frac{3 \left(\frac{da}{dx} \right)^2 - 2a \frac{d^2a}{dx^2}}{\left(\frac{da}{dx} \right)^2}.$$

If in the diagram we think all the values of x present, e.g. ascending from the value of x for which $\frac{da}{dx} = 0$, this locus is a curve

with an asymptote for the value of x , for which $\frac{da}{dx} = 0$, and it has

a minimum volume for the value of x , for which $\left(\frac{da}{dx} \right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$.

For greater values of x the volume increases.

If in $\frac{db}{v-b} = \frac{da}{2a}$ the value $3b$ is put for v , we find $\frac{1}{b} \frac{db}{dx} = \frac{1}{a} \frac{da}{dx}$.

But then not only $\frac{d^2p}{dv dx} = 0$ in the equation $\frac{d^3p dv}{dv^2 dx} + \frac{d^2p}{dv dx} = 0$, but also $\frac{d^2p}{dv^2}$. The value of $\frac{dv}{dx}$ is then indefinite, and at the temperature at which this takes place, and which is the minimum temperature represented by $\frac{8}{27} \frac{a_x}{b_x}$, the curve $\frac{dp}{dv}$ has two branches, which intersect in the point given by $v = 3b$ and x , belonging to $\frac{1}{b} \frac{db}{dx} = \frac{1}{a} \frac{da}{dx}$. For higher values of v , e.g. $v = 4b$, the point of intersection of the two curves lies on the vapour branch of $\frac{dp}{dv} = 0$, and vice versa. If we

write $v = nb$, the form $\frac{2}{n-1} = \frac{\frac{1}{a} \frac{da}{dx}}{\frac{1}{b} \frac{db}{dx}}$ follows from $\frac{\frac{db}{dx}}{v-b} = \frac{\frac{da}{dx}}{2a}$. For

those values of x for which the numerator is smaller than the denominator $n > 3$, and vice versa. Only if also $\frac{da}{dx} = 0$ should occur in the diagram, the value of n , and so also of v , is infinite.

If we determine the point in which the two curves touch, we shall find the same point in which $\frac{d^3p}{dv dx}$ has the minimum volume; for as the curve $\frac{dp}{dv} = 0$ has a tangent parallel to the X -axis in every point of intersection, also the curve $\frac{d^2p}{dv dx} = 0$ must have such a tangent in case of contact.

The condition that for a point of the last-mentioned curve $\frac{dv}{dx} = 0$ is $\frac{d^2p}{dv dx^2} = 0$. So we have

$$\frac{dp}{dv} = 0 \quad \text{or} \quad \frac{MRT}{(v-b)^2} = \frac{2a}{v^3}$$

$$\frac{d^2p}{dv dx} = 0 \quad \text{or} \quad \frac{MRT \frac{db}{dx}}{(v-b)^3} = \frac{da}{v^3}$$

and

$$\frac{d^2p}{dv dx^2} = 0 \quad \text{or} \quad 3 \frac{MRT \left(\frac{db}{dx}\right)^2}{(v-b)^4} = \frac{d^2a}{v^3}$$

By comparing the square of the second of these equations with the product of the two others, we find back the condition:

$$\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}.$$

If we put $a = A + 2Bx + Cx^2$, in which $A = a_1$, $B = a_{12} - a_1$, and $C = a_1 + a_2 - 2a_{12}$, this equation leads to:

$$(B + Cx)^2 + \frac{B^2 - AC}{2} = 0$$

or

$$B + Cx = + \sqrt{\frac{a_1 a_2 - a_{12}^2}{2}}.$$

The positive sign before the radical sign is required by the condition that $\frac{da}{dx}$ must be positive. If x is to be real, $a_1 a_2$ must be $> a_{12}^2$, and the condition that x lies between 0 and 1 is indicated by the construction of fig. 33. Let OO' be the x -axis, and let PQ be

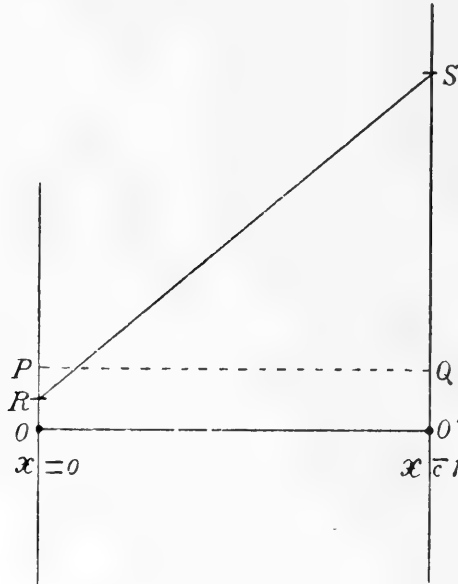


Fig. 33.

drawn at the height of $\sqrt{\frac{a_1 a_2 - a_{12}^2}{2}}$. Let us then take $OR = a_{12} - a_1$ and $O'S = a_2 - a_{12}$, then the point of intersection of RS and

PQ will have to lie between $x = 0$ and $x = 1$ for the condition $\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$ to be fulfilled in the diagram.

According to the result arrived at in Contribution VII with regard to the point in which $\left(\frac{dp}{dx}\right)_v = 0$ touches the line $\left(\frac{dp}{dv}\right)_x = 0$, the value of x in which $\left(\frac{da}{dx}\right)^3 = \frac{2}{3} a \frac{d^2a}{dx^2}$ must lie not very far from this point of contact.

But whether it might not even lie to the right of that value of x , for which $\frac{a_x}{b_x}$ has a minimum value, can only appear from a direct investigation. Then it may appear at the same time whether in case of contact of the two curves $\frac{dp}{dv} = 0$ and $\frac{d^2p}{dv dx} = 0$ the temperature has maximum value or minimum value.

Let us eliminate the value of v from the equations of the two curves. Among others we may do this by substituting the value of

v from $\frac{2 \frac{db}{dx}}{v-b} = \frac{1}{a} \frac{da}{dx}$ in $\frac{d^2p}{dv dx} = 0$. Let us write :

$$\frac{v-b}{b} = 2 \frac{\frac{1}{b} \frac{db}{dx}}{\frac{1}{a} \frac{da}{dx}} = 2z,$$

or

$$\frac{v}{b} = 1 + 2z,$$

and

$$\frac{b}{v} = \frac{1}{1+2z},$$

and

$$1 - \frac{b}{v} = \frac{2z}{1+2z}.$$

From $\frac{d^2p}{dv dx} = 0$ follows :

$$1 - \frac{b}{v} = \frac{\sqrt[3]{MRT \frac{db}{dx}}}{\frac{da}{dx}}.$$

Hence :

$$\sqrt[3]{MRT \frac{db}{dx}} \frac{da}{dx} = \frac{2z}{1+2z}$$

Differentiating logarithmically, we get :

$$\frac{1}{3T} \frac{dT}{dx} - \frac{1}{3} \frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}} = \frac{1}{z} \frac{da}{dx} \frac{1}{1+2z}$$

Now

$$\frac{1}{z} \frac{dz}{dx} = \frac{1}{a} \frac{da}{dx} - \frac{1}{b} \frac{db}{dx} - \frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}$$

or

$$\frac{1+2z}{3T} \frac{dT}{dx} - \frac{1}{3} \frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}} (1+2z) = \frac{1}{a} \frac{da}{dx} - \frac{1}{b} \frac{db}{dx} - \frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}$$

or

$$\frac{1+2z}{3T} \frac{dT}{dx} + \frac{2}{3} \frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}} (1-z) = \frac{1}{a} \frac{da}{dx} - \frac{1}{b} \frac{db}{dx}$$

or

$$\frac{1+2z}{3T} \frac{dT}{dx} = \left[\frac{1}{a} \frac{da}{dx} - \frac{1}{b} \frac{db}{dx} \right] \left[1 - \frac{2}{3} \frac{a \frac{d^2a}{dx^2}}{\left(\frac{da}{dx}\right)^2} \right]$$

So the value $\frac{dT}{dx}$ is equal to 0, first if $\frac{1}{a} \frac{da}{dx} = \frac{1}{b} \frac{db}{dx}$, and secondly if $\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$. If, when drawing T as function of x , we begin with small values of x , and if we should admit also negative values of x into our consideration, then both factors in the expression for $\frac{dT}{dx}$ are negative e. g. for $\frac{da}{dx} = 0$, and so $\frac{dT}{dx}$ is positive. If x increases a value of x is reached for which one of these factors becomes equal

to 0. For still higher value of x the second factor becomes equal to 0. Between these two special values of x , $\frac{dT}{dx}$ is negative — and for values of x which are larger than that for which also the second factor is zero, $\frac{dT}{dx}$ is again positive. So the value of T presents a maximum and a minimum.

In general we must now put two cases as possible according as the value of x for which $\frac{1}{a} \frac{da}{dx} = \frac{1}{b} \frac{db}{dv}$, is smaller or larger than that for which $\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$. The intermediate case in which these two values would coincide, might be considered as a third possibility. Let us call the maximum value of the temperature T_M , and the minimum value T_m . For a value of T below T_m there is only one point of intersection of $\frac{dp}{dv} = 0$ and $\frac{d^2p}{dvd^2x} = 0$, namely at small value of x . For values of T above T_M there is also only one point of intersection for large value of x . But for values of T between T_m and T_M there are three points of intersection. Of these three points of intersection there is always one, the middle one, which lies at a value of x lying between that which makes the first factor equal to zero, and that which makes the second factor equal to zero.

To give a survey of the course of the points of intersection of $\frac{dp}{dv} = 0$ and $\frac{d^2p}{dvd^2x} = 0$ at different temperatures, and so of the circumstances for which $\frac{dp}{dv} = 0$ has a maximum or minimum volume, we shall have to separately treat the cases for the different situation of the two values of x , for which $\frac{1}{a} \frac{da}{dx} = \frac{1}{b} \frac{db}{dv}$, and $\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$.

Let us first take the case for which the value of x for minimum value of $\frac{a_x}{b_x}$ is the smallest. This case is the simplest, and was discussed by me already before. Then a curve $\frac{d^2p}{dvd^2x} = 0$ indicated in fig. 34 by α , passes through the double point of $\frac{dp}{dv} = 0$. For lower T , α has assumed the position β , and $\frac{dp}{dv} = 0$ the position γ , so that there are then two points of intersection (1 and 2) to be found.

But at higher T these points of intersection exist no longer; then the line $\frac{d^2p}{dvdx} = 0$ runs between the two branches in which $\frac{dp}{dv} = 0$ has split up, without intersecting them, at least at this place. There

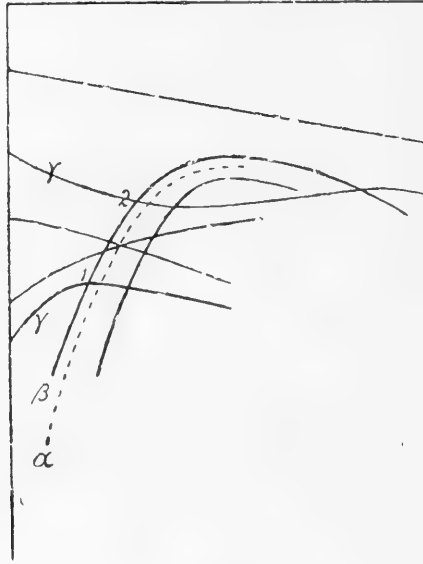


Fig. 34.

is, however, still a point of intersection, but at much greater value of x , namely a point of intersection formed by the branch of $\frac{d^2p}{dvdx} = 0$ which runs again to larger volumes. In this point of inter-

section the righthand branch of $\frac{dp}{dv} = 0$ has again minimum volume.

So for values of T below that of the double point of $\frac{dp}{dv} = 0$, the

branch of the liquid volumes of $\frac{dp}{dv} = 0$ has two points of intersection

with $\frac{d^2p}{dvdx} = 0$, so a maximum and a minimum volume, and for

much smaller value of x there is then a minimum volume on the vapour branch. If we lower T still further, maximum and minimum volume of the liquid branch draw nearer to each other, and they

coincide at the value of x for which $\left(\frac{da}{dx}\right)^2 = \frac{2}{3}a \frac{d^2a}{dx^2}$. Then the vapour

branch has two coinciding values of x , for which $\frac{dv}{dx} = 0$, and so also a point of inflection, namely for the volume that is the smallest volume for which a point of intersection of the two curves exists. At still lower temperature the liquid branch has no longer a point of intersection; but the point of intersection of the vapour branch continues to exist, and proceeds continually to smaller value of x . I need hardly point out that in this description negative values of x are again not considered as unreal. The condition for a point occurring on the curve $\frac{dp}{dv} = 0$ in which $\frac{dv}{dx} = 0$ and $\frac{d^2v}{dx^2} = 0$ is found from:

$$\frac{d^2p}{dv^2} \frac{dv}{dx} + \frac{d^2p}{dv dx} = 0$$

and

$$\frac{d^2p}{dv^2} \frac{d^2v}{dx^2} + \frac{d^2p}{dv^3} \left(\frac{dv}{dx} \right)^2 + 2 \frac{d^2p}{dv dx} \left(\frac{dv}{dx} \right) + \frac{d^3p}{dv dx^2} = 0.$$

Hence besides $\frac{dp}{dv} = 0$, also $\frac{d^2p}{dv dx} = 0$ and $\frac{d^3p}{dv dx^2} = 0$.

Let us now consider the second case, for which the value of x corresponding to $\left(\frac{da}{dx} \right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$, is the smallest. For this value of x the value of T is then maximum, and the temperature for the double point of $\frac{dp}{dv} = 0$ will be a minimum. This means that with decrease of T two points of intersection *vanish*, whereas in the preceding case two new points of intersection *appear* with decrease of T .

Let us first consider this minimum temperature; then a curve $\frac{d^2p}{dv dx} = 0$ passes through the double point, which, in this point, may be considered to have two points in common with the line $\frac{dp}{dv} = 0$, and which has a third point of intersection for smaller value of x . This third point of intersection is to be found on the vapour branch of the lefthand branch of $\frac{dp}{dv} = 0$, because it has smaller x . Fig. 35 indicates the places of the three points of intersection for this value of T . With decrease of T two of the points of intersection lie on the vapour branch of the lefthand branch of the line $\frac{dp}{dv} = 0$, and a

third point of intersection on the liquid branch of the other branch. With increase of T the two points of intersection on the left-hand branch coincide in the point for which x is found from $\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$. Everything shows that at the temperature of the double point that part of the line $\frac{d^2p}{dv dx} = 0$ runs through the double

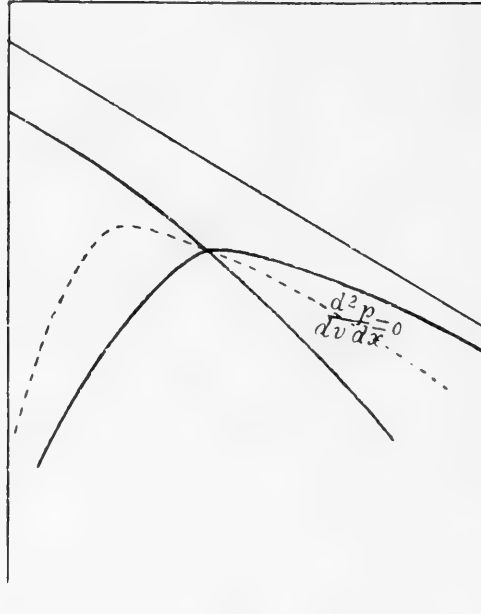


Fig. 35.

point that lies beyond the minimum volume. With T lower than that of the double point this part of the curve remains entirely in the unstable region.

If we try to ascertain on what it depends whether the value of x which corresponds to $\frac{1}{a} \frac{da}{dx} = \frac{1}{b} \frac{db}{dx}$ is smaller or larger than that for which $\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$ we may, to decide this, substitute the value of x which follows from the second of these equations, in :

$$b \frac{da}{dx} - a \frac{db}{dx}.$$

If we then find a positive value for this form, the first case

holds; then the point where $\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$ lies in the region where the value of $\frac{a}{b}$ again increases.

Eliminating a we may also write for $b \frac{da}{dx} - a \frac{db}{dx}$:

$$\frac{da}{dx} \left\{ b - \frac{3}{2} \frac{db}{dx} \frac{\frac{da}{dx}}{\frac{d^2a}{dx^2}} \right\}$$

and as $\frac{da}{dx}$ must be positive, just as $\frac{d^2a}{dx^2}$, the sign depends on:

$$\frac{2}{3} b \frac{d^2a}{dx^2} - \frac{3}{2} \frac{db}{dx} \frac{da}{dx}.$$

And if we put $b_2 = nb_1$, $a = A + 2Bx + Cx^2$, this form becomes:

$$\frac{2}{3} C [1 + (n-1)x] - (n-1) [B + Cx]$$

or

$$\frac{2}{3} C + \frac{2}{3} (n-1) Cx - (n-1) (B + Cx)$$

or

$$\frac{2}{3} \frac{C}{n-1} - \frac{2}{3} B - \frac{B+Cx}{3}$$

Now we have found above $B + Cx = + \sqrt{\frac{a_1 a_2 - a_{12}^2}{2}}$, and as $B = a_{12} - a_1$ and $C = a_1 + a_2 - 2a_{12}$, the sign depends on:

$$\frac{a_1 + a_2 - 2a_{12}}{n-1} - (a_{12} - a_1) - \frac{1}{2} \sqrt{\frac{a_1 a_2 - a_{12}^2}{2}}.$$

If this sign is positive we have the case treated first. So for this case

$$\frac{(a_2 - a_{12}) - (a_{12} - a_1)}{a_{12} - a_1} > n - 1$$

or

$$\frac{a_2 - a_{12}}{a_{12} - a_1} > n.$$

is certainly necessary, but not sufficient.

With the following numerical values the conditions necessary for the first case, and the condition that the two values of x occur in the diagram, are satisfied.

Let $n = 5$, $a_1 = 1$, $a_2 = 30$ and $a_{12} = 2$. The value of x satisfying $\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$, is found from :

$$(a_{12} - a_1) + (a_1 + a_2 - 2a_{12})x = \sqrt{\frac{a_1 a_2 - a_{12}^2}{2}}$$

or

$$1 + 27x = \sqrt{13} = 3,6$$

or

$$x_1 = \frac{2,6}{27}.$$

The value of x satisfying $\frac{1}{a} \frac{da}{dx} = \frac{1}{b} \frac{db}{dx}$, is found from the equation :

$$B - \frac{n-1}{2} A + Cx + \frac{n-1}{2} Cx^2$$

or

$$-1 + 27x + 54x^2 = 0$$

or

$$x_2 = 0,035.$$

If we had put $a_2 = 10$, leaving the other values unchanged, so that $\frac{a_2 - a_{12}}{a_{12} - a_1} > n$ still remains larger than x , we find x_1 from the equation :

$$1 + 7x_1 = \sqrt{3} \text{ and } x_1 = 0,1045$$

and x_2 from the equation :

$$-1 + 7x_2 + 14x_2^2 = 0$$

or

$$x_2 = -\frac{1}{4} + \sqrt{\frac{1}{14}}$$

$$4x_2 = -1 + \sqrt{\frac{15}{7}} \text{ and } x_2 = 0,116$$

And finally, let us take a numerical example, more in agreement with those which occur in the cases of minimum plaitpoint temperature studied experimentally. Let $n = 1,5$, $a_1 = 1$, $a_2 = 1,45$, so that $T_{k_2} < T_{k_1}$. Let further $a_{12} = 1,1$. Then x_1 is found from the equation :

$$0,1 + 0,25x = \sqrt{0,12} = 0,3435 \dots$$

$$x_1 = 0,974$$

and x_2 from the equation :

$$- 0,15 + 0,25x + \frac{1}{4} 0,25 x^2 = 0$$

or x_1 nearly equal to 0,5.

Here we very clearly get back the first case.

The intermediate case would require that x_1 should be equal to x_2 . If we wish to direct our attention to other particularities of the intermediate case, we observe: 1. that then there is only one point

of intersection for $\frac{dp}{dv} = 0$ and $\frac{d^2p}{dv dx} = 0$ at every temperature;

2. that then at the double point of $\frac{dp}{dv} = 0$ one of the branches must have a tangent parallel to the X -axis; and so, the two values of $\frac{dv}{dx}$ for that double point being given by the equation:

$$\frac{d^3p}{dv^3} \left(\frac{dv}{dx} \right)^2 + 2 \frac{d^2p}{dv^2 dx} \left(\frac{dv}{dx} \right) + \frac{d^2p}{dv dx^2} = 0$$

$\frac{d^3p}{dv dx^2}$ is again equal to zero (see page 195). The curve $\frac{d^2p}{dv dx} = 0$

now does not pass through the double point either with its descending, nor with its ascending branch, but has there minimum volume. At

lower temperature the vapour branch of $\frac{dp}{dv} = 0$ is cut in a point with

somewhat lower value of x , and at higher temperature the liquid branch of the righthand branch is intersected with slightly higher

value of x . Just at the temperature of the double point $\frac{d^2p}{dv dx} = 0$

touches with a tangent parallel to the X -axis.

If more in general, we wish to determine what the ratio of

$\frac{\left(\frac{da}{dx} \right)^3}{\frac{d^2a}{a dx^2}} = m$ is at that value of x for which $\frac{a_x}{b_x}$ has minimum value, we

may take the following course. From:

$$b \frac{da}{dx} = a \frac{db}{dx}$$

we derive:

$$[1 + (n-1)x][B + Cx] = \frac{n-1}{2}(A + 2Bx + Cx^2)$$

or

$$x^2 + \frac{2}{n-1}x + \frac{\frac{2}{n-1}B - A}{C} = 0$$

and so

$$x = -\frac{1}{n-1} + \sqrt{\left[\frac{1}{(n-1)^2} - \frac{B}{C}\right]^2 + \frac{AC - B^2}{C^2}}$$

From $\left(\frac{da}{dx}\right)^2 = ma \frac{d^2a}{dx^2}$ we derive:

$$(2-m)(B + Cx)^2 = m(AC - C^2)$$

or

$$x + \frac{B}{C} = \sqrt{\frac{m}{2-m} \frac{AC - B^2}{C^2}}$$

By equating the two values of x thus obtained, we find the equation:

$$\frac{B}{C} - \frac{1}{n-1} + \sqrt{\left[\frac{1}{(n-1)^2} - \frac{B}{C}\right]^2 + \frac{AC - B^2}{C^2}} = + \sqrt{\frac{m}{2-m} \frac{AC - B^2}{C^2}}$$

from which follows:

$$\frac{AC - B^2}{C^2} = + 2 \left[\frac{1}{n-1} - \frac{B}{C}\right] \sqrt{\frac{m}{2-m} \frac{AC - B^2}{C^2}} + \frac{m}{2-m} \frac{AC - B^2}{C^2}$$

or

$$\frac{1-m}{2-m} \sqrt{\frac{AC - B^2}{C^2}} = \left[\frac{1}{n-1} - \frac{B}{C}\right] \sqrt{\frac{m}{2-m}}$$

or

$$\frac{1-m}{\sqrt{m(2-m)}} \sqrt{\frac{AC - B^2}{C^2}} = \frac{1}{n-1} - \frac{1}{\frac{a_2 - a_{12}}{a_{12} - a_1} - 1} = \frac{\frac{a_2 - a_{12}}{a_{12} - a_1} - n}{(n-1) \left(\frac{a_2 - a_{12}}{a_{12} - a_1} - 1\right)}$$

or

$$\frac{1-m}{\sqrt{m(2-m)}} \frac{\sqrt{(a_1 a_2 - a_{12}^2)}}{a_{12} - a_1} = \frac{\frac{a_2 - a_{12}}{a_{12} - a_1} - n}{n-1}$$

In particular it appears that $m = 1$, if $\frac{a_2 - a_{12}}{a_{12} - a_1} = n$; and if $\frac{a_2 - a_{12}}{a_{12} - a_1}$

should be $\geq n$, then $m \leq 1$, at least if $a_{12} > a_1$.

If m is known for certain value of x , the decrease or increase of m may be derived from the equation:

$$(2-m)a = \text{constant},$$

which constant is equal to zero, if $a_1 a_2 = a_{12}^2$, and has else the sign of $a_1 a_2 - a_{12}^2$.

Physics. — “*Contribution to the theory of binary mixtures.*” IX.

By Prof. J. D. VAN DER WAALS.

THE INTERSECTION OF $\left(\frac{dp}{dx}\right)_v = 0$ AND $\left(\frac{d^2\psi}{dx^2}\right)_v = 0$.

As in previous communications we shall write the equation of $\left(\frac{dp}{dx}\right)_v = 0$ in the form $\frac{MRT}{(v-b)^2} \frac{db}{dx} = \frac{da}{dx} \frac{1}{v^2}$, and the equation of $\left(\frac{d^2\psi}{dx^2}\right)_o = 0$ in the form:

$$MRT \left\{ \left(\frac{1}{x(1-x)} \right) + \left(\frac{db}{dx} \right)^2 \frac{1}{(v-b)^2} \right\} = \frac{d^2a}{v \frac{dx^2}}{v}$$

Then the locus of the points of intersection is given by the equation:

$$(v-b)^2 + \left(\frac{db}{dx} \right)^2 x(1-x) = x(1-x) \frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}} v \frac{db}{dx}$$

or

$$(v-b)^2 - x(1-x) \frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}} \frac{db}{dx} (v-b) + x(1-x) \left[\frac{db}{dx} - b \frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}} \right] = 0.$$

The factor of the known term of this equation: $\frac{\frac{db}{dx} \frac{da}{dx} - b \frac{d^2a}{dx^2}}{\frac{da}{dx}}$

may be written in the form:

$$\frac{db}{dx} \frac{B - \frac{C}{n-1}}{B + Cx},$$

if $b = b_1(1-x) + b_2x$, and $a = A + 2Bx + Cx^2$ be put, and the equation itself may be given in the form:

$$\left(\frac{db}{dx} \right)^2 - x(1-x) \frac{C}{B+Cx} \frac{(v-b)}{\frac{db}{dx}} + x(1-x) \frac{B - \frac{C}{n-1}}{B+Cx} = 0.$$

When $B - \frac{C}{n-1}$ is negative, this equation has certainly a positive root, when viz. the quantity $B + Cx$ is positive, which is required for the occurrence of the line $\left(\frac{dp}{dx}\right)_v = 0$. The negative root is without significance for the problem. The quantity $\left(\frac{C}{n-1} - B\right)$ positive may be written as follows:

$$(a_{12} - a_1) \frac{\frac{a_2 - a_{12}}{n-1} - n}{a_{12} - a_1} > 0.$$

Let us call the case $\frac{a_2 - a_{12}}{a_{12} - a_1} < n$ the first case, and $\frac{a_2 - a_{12}}{a_{12} - a_1} > n$ the second case.

In the first case the quadratic equation in $\frac{v-b}{\frac{db}{dx}}$ has the factor of the first power of $(v-b)$ negative, and the known term positive. Two real positive values of $v-b$ can then satisfy this equation. These roots are however real only if:

$$x^2 (1-x)^2 \left(\frac{C}{B+Cx}\right)^2 \geq 4x(1-x) \frac{B - \frac{C}{n-1}}{B+Cx},$$

or

$$x(1-x) \geq \left(\frac{B}{C} - \frac{1}{n-1}\right) \frac{B+Cx}{C}.$$

So the roots are imaginary if:

$$x^2 - x \left\{ 1 - 4 \left(\frac{B}{C} - \frac{1}{n-1}\right) \right\} + 4 \frac{B}{C} \left(\frac{B}{C} - \frac{1}{n-1}\right) > 0.$$

For values of x which are nearly 0 or nearly 1, they are therefore imaginary. From this follows that the locus of the points of intersection of $\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{d^2\psi}{dx^2}\right)_v = 0$ is a closed curve in the first case. By dividing by $x(1-x)$ we have only lost the values $x=0$ and $x=1$, which, however, only correspond to $v-b=0$ and $T=0$. This closed curve can contract to a single point, and even disappear altogether. Contraction to a single point takes place, if:

$$\left\{ 1 - 4 \left(\frac{B}{C} - \frac{1}{n-1} \right) \right\}^2 = 16 \frac{B}{C} \left(\frac{B}{C} - \frac{1}{n-1} \right),$$

or if

$$1 - 8 \left(\frac{B}{C} - \frac{1}{n-1} \right) - \frac{16}{n-1} \left(\frac{B}{C} - \frac{1}{n-1} \right) = 0,$$

or

$$\frac{B}{C} - \frac{1}{8} \frac{(n+3)^2}{n^2-1},$$

or

$$\frac{a_2 - a_{12}}{a_{12} - a_1} = 1 + 8 \frac{n^2 - 1}{(n+3)^2},$$

or

$$\frac{a_2 - a_{12}}{a_{12} - a_2} - n = - (n-1) \left\{ 1 - \frac{8(n+1)}{(n+3)^2} \right\}.$$

In this expression the value of the factor $n-1$ always lies between 0 and 1 for values of n between 1 and ∞ . For values of $\frac{a_2 - a_{12}}{a_{12} - a_2} < 1 + 8 \frac{n^2 - 1}{(n+3)^2}$ the locus is imaginary.

The point at which the locus disappears, lies at $x = \frac{n+3}{(4n+1)}$

and so always between $\frac{1}{2}$ and $\frac{1}{4}$, and at $v-b = \frac{\frac{db}{dx} n - 1}{4n+1}$ or $v = \frac{b_1 + b_2}{2}$.

By substitution in $\left(\frac{dp}{dx} \right)_v = 0$ we find the value of MRT equal to:

$$MRT = \frac{(a_1 + a_2 - 2a_{12})(n-1)^3 (n+3) (3n+1)}{b_2 - b_1 \cdot 16 (n+1)^5}.$$

This is not the point in which the curve $\frac{d^2\psi}{dx^2} = 0$ disappears. Already the circumstance that the latter curve disappears between $x = \frac{1}{3}$ and $x = \frac{1}{2}$, whereas in the same cases the discussed point

disappears between $x = \frac{1}{4}$ and $x = \frac{1}{2}$, shows this. We may, however conclude, from this, that as n draws nearer to 1, the two points will approach each other as regards the value of x .

Thus (cf. Contribution III These Proc. IX p. 829) $x_g = 0,48$ for $\frac{1}{n-1} = 5,04$, whereas with $x = \frac{n+3}{4(n+3)}$ nearly 0,477 is found. But

the value of v is much smaller for the point discussed here than for the point in which the curve $\frac{d^2\psi}{dx^2} = 0$ disappears.

We should have to expect à priori that these two points differ. Let us imagine $\frac{d^2\psi}{dx^2} = 0$ for different values of T as a surface with the axes x, v and T , and let the T -axis be the vertical axis. Then this is a surface with the whole v, x -plane as basis, with top at $T = T_g$. Let us also imagine $\frac{dp}{dx} = 0$ as surface construed on the same axes, then the sections of this surface pass to larger x and larger v with ascending values of T . Now this latter surface cannot pass through the top of $\frac{d^2\psi}{dx^2} = 0$ without yielding other points of intersection, a curve of intersection. If it can touch in the top, then it would be possible that this curve of intersection did not exist. But a tangent plane to $\frac{d^2\psi}{dv^2} = 0$ runs parallel to the x, v -plane, and such a tangent plane $\frac{dp}{dx} = 0$ has not.

That a tangent plane in the top of $\frac{d^2\psi}{dx^2} = 0$ runs parallel to the x, v -plane, follows from :

$$\frac{d^3\psi}{dx^2 dT} dT + \frac{d^3\psi}{dx^3} dx + \frac{d^3\psi}{dx^2 dv} dv = 0.$$

In the top $\frac{d^3\psi}{dx^3}$ and $\frac{d^3\psi}{dx^2 dv}$ are both equal to zero, whereas $\frac{d^3\psi}{dx^2 dT}$ is not equal to 0; hence $\frac{dT}{dx}$ and $\frac{dT}{dv}$ is zero, or the tangent plane parallel to the v, x -plane.

As soon as $\frac{a_2 - a_{12}}{a_{12} - a_1}$ is not only smaller than n , but also smaller than $1 + 8 \frac{n^2 - 1}{(n + 3)^2}$, the two curves do not intersect at any temperature. If on the other hand $\frac{a_2 - a_{12}}{a_{12} - a_1} < n$, and $> 1 + 8 \frac{n^2 - 1}{(n + 3)^2}$, the two surfaces $\frac{d^2\psi}{dx^2} = 0$ and $\frac{dp}{dx} = 0$ intersect in such a way that the projection of the section is a closed curve; the section itself lies then

on the side of the small volumes of $\frac{d^2\psi}{dx^2} = 0$, and between two low temperatures. If we denote these temperatures by T_1 and T_2 , then contact does not begin before T_1 ; between T_1 and T_2 there is intersection, and at T_2 there is again contact. So at T_1 the curve $\frac{dp}{dx} = 0$ proceeds more rapidly towards larger volumes with rise of temperature, but at T_2 on the contrary, the curve $\frac{d^2\psi}{dx^2} = 0$.

In agreement with fig. 24 (Contribution V p. 134) the value of x for the minimum volume of $\frac{dp}{dx} = 0$ is then smaller than that of the points of contact; and the point to which the locus of the points of contact contracts lies then on that portion of $\frac{dp}{dx} = 0$ that proceeds to greater volumes with increasing x .

We may verify this by showing that $\left(\frac{d^2p}{dx^2}\right)_v$ is *positive* for this

point. As $\left(\frac{d^2p}{dx^2}\right)_v = 2 \frac{MRT \left(\frac{db}{dx}\right)^2}{(v-b)^3} - \frac{d^2a}{v^3}$, for a point of $\left(\frac{dp}{dx}\right)_v$, or for

which $\frac{MRT \frac{db}{dx} \frac{da}{dx}}{(v-b)^2} = \frac{da}{v^3}$, the sign of $\left(\frac{d^2p}{dx^2}\right)_v$ will depend on:

$$\frac{\frac{db}{dx}}{v-b} - \frac{\frac{d^2a}{dx^2}}{2 \frac{da}{dx}}$$

or on

$$\frac{\frac{da}{dx}}{\frac{d^2a}{dx^2}} - \frac{1}{2} \frac{v-b}{\frac{db}{dx}}$$

or on

$$\left(\frac{B}{C} + x\right) - \frac{1}{2} \frac{v-b}{\frac{db}{dx}}$$

If, as was found above, we take $\frac{B}{C} = \frac{1}{8} \frac{(n+3)^2}{n^2-1}$ and $x = \frac{n+3}{4(n+1)}$

and so $\frac{B}{C} + x = \frac{1}{8} \frac{(n+3)(3n+1)}{n^2-1}$, while $\frac{1}{2} \frac{v-b}{\frac{db}{dx}} = \frac{1}{8} \frac{n-1}{n+1}$, it is at

once evident that the sign is certainly positive.

We can now get an insight into the way in which increase of the value of $\frac{a_2 - a_1}{a_1 - a_2}$ influences the intersection of the two surfaces $\frac{d^2\psi}{dx^2} = 0$ and $\frac{dp}{dx} = 0$. If this quantity, which I shall represent by k ,

is smaller than $1 + 8 \frac{n^2-1}{(n+3)^2}$, no intersection is possible. In this

consideration we shall leave n and C invariable, and so keep $\frac{d^2\psi}{dx^2} = 0$

unchanged. If we now make k increase, $\frac{dp}{dx} = 0$ will vary and

intersect the surface $\frac{d^2\psi}{dx^2} = 0$. When $k < n$, this intersection takes

place in a closed curve. As well in the v, x -projection as in the T, x -projection and in the v, T -projection we may speak of a lower and an upper branch. But these branches do not extend over the whole width from $x = 0$ to $x = 1$. With approach of k to n the width of this section becomes larger, but the lower branch descends continually, and the upper branch ascends. In the v, x -projection this implies that the branch with the lower value of v approaches b , and that the upper branch assumes a higher value of v . In the T, x -projection this means that T verges to zero for the lower branch, and increases for the upper branch, but still remains very far below the value of T_q (See Contribution III These Proc. IX p. 830). And finally when k has become equal to n , the closed curve of the section extends from $x = 0$ to $x = 1$, but the lower branch coincides with the line $v = b$, and the value of T for this branch is the absolute zero-point. For the upper branch v and T have constantly increased. And the question rises whether then the whole section is still found on what I shall call the back side for the surface $\frac{d^2\psi}{dx^2} = 0$; i. e. the points with the smaller value of v . We shall presently revert to this question. But already now it is to be seen what will be the consequence of increase of k above n .

The process we described above, goes on. The lower branch does not become imaginary, but has values of $v < b$ and values of T which are again positive. So they are of no importance for the real

problem; and as soon as $k > n$ we have only to occupy ourselves with a single branch for the section. This is also immediately seen from the quadratic equation in $v-b$ of p. 201, which has then one negative, and one positive root. So if $k > n$, we may say that the two surfaces intersect in a curve which has only one branch. For $x=0$ and $x=1$ the value of v is always equal to b , and that of T always equal to 0. From this follows already that there will be question of a maximum value of T for the section. For this value of T the two curves will touch at given value of T , viz. $\left(\frac{d^2\psi}{dx^2}\right)_{vT} = 0$

and $\left(\frac{dp}{dx}\right)_{vT} = 0$. We have also met with such a contact in the case $k < n$, and we then concluded that the contact took place as is represented in fig. 24^c (Contribution V p. 134).

But another contact is possible, namely such a contact for which the curve $\left(\frac{d^2\psi}{dx^2}\right)_{vT} = 0$ lies in the region where $\left(\frac{dp}{dx}\right)_{vT}$ is positive everywhere except at the point of contact, or as we might also express it, outside $\left(\frac{dp}{dx}\right)_{vT} = 0$. This would imply for the intersection of the two surfaces, that the common curve which runs upwards from $x=0$, and $x=1$ and $T=0$, passes round the top of $\left(\frac{d^2\psi}{dx^2}\right)_{vT} = 0$, or that it remains entirely on the side of the small volumes, as was the case up to now.

In the gradual transformation of the common line of intersection which is due to the increase of k above n , it must, therefore, have passed through the top of $\frac{d^2\psi}{dx^2} = 0$ for certain value of k . And we shall now treat the condition for this circumstance. Properly speaking I have already tried to solve this problem in Contribution III p. 834, to which I refer for the meaning of the following formula. The circumstance that the curve of intersection passes through the top is given by:

$$\frac{d^2a}{dx^2} (1-2x_g) = \frac{da}{dx} 4y_g^2.$$

But I shall adapt the discussion of this formula to the systematic treatment of this paper.

If we put the value $\frac{(1-2x_g)^2}{4x_g(1-x_g)}$ for y_g^2 (see Cont. III p. 832) this

equation may assume the following form :

$$\frac{B}{C} = \frac{x_g(3x_g-1)}{1-2x_g} - \frac{1}{n-1}.$$

This equation may also be derived by the following consideration.

If the top of $\frac{d^2\psi}{dx^2} = 0$ is also to be a point of $\frac{dp}{dx} = 0$, the following

equations are to be satisfied: $\frac{d^2\psi}{dx^2} = 0$, $\frac{d^3\psi}{dx^3} = 0$, $\frac{d^3\psi}{dx^3} = 0$, and

$\frac{d^2\psi}{dx^2} = 0$. It appears from this, that not only $\frac{dp}{dx} = 0$ is to be satisfied

but also $\frac{d^2p}{dx^2} = 0$. This means that the point of the curve $\left(\frac{dp}{dx}\right)_{vI} = 0$

at which this curve has its minimum volume, must pass through the top. So the following equations must be satisfied :

$$\frac{MRT \frac{db}{dx}}{(v-b)^2} = \frac{da}{v^2}$$

and

$$2 \frac{MRT \left(\frac{db}{dx}\right)^2}{(v-b)^3} = \frac{d^2a}{v^2}$$

and so also

$$\frac{v-b}{2 \frac{db}{dx}} = \frac{\frac{da}{dx}}{\frac{d^2a}{dx^2}} = \frac{B}{C} + x$$

Now for the top of $\frac{d^2\psi}{dx^2} = 0$ (Contribution III p. 829) the equation

$$2 \left(\frac{db}{dx}\right) = \sqrt[3]{\frac{x_g^2(1-x_g)^2}{4(1-2x_g)}} \text{ en } \frac{1}{n-1} = \frac{x_g^2}{1-2x_g} - \sqrt[3]{\frac{x_g^2(1-x_g)^2}{4(1-2x_g)}}$$

holds. Hence :

$$\frac{B}{C} + x_g = \frac{x_g^2}{1-2x_g} - \frac{1}{n-1}$$

or

$$\frac{B}{C} = \frac{x_g(3x_g-1)}{1-2x_g} - \frac{1}{n-1}.$$

If it were possible to express x_g as explicit function of n , it would

directly appear, that k must be $> n$ to satisfy the circumstance that $\frac{dp}{dx} = 0$ shall pass through the top. Now we shall have to content ourselves with calculating the value of k for different values of n with the aid of the table (p. 829). Thus $\frac{1}{n-1} = 0,3704$ corresponds to $x_g = 0,4$, and we find $\frac{B}{C}$ then equal to $0,4 - 0,3704 = 0,0296$. As $\frac{B}{C} = \frac{1}{k-1}$, we find $k = 1 + \frac{1}{0,0296}$, n being $= 1 + \frac{1}{0,3704}$. Thus we find:

x_g	n	k
0,4	$1 + \frac{1}{0,37}$	$1 + \frac{1}{0,03}$
0,45	$1 + \frac{2}{3}$	$1 + \frac{1}{0,075}$
0,46	$1 + \frac{1}{2,08}$	$1 + \frac{1}{0,105}$
0,47	$1 + \frac{1}{3,06}$	$1 + \frac{1}{0,15}$
0,48	$1 + \frac{1}{5,04}$	$1 + \frac{1}{0,24}$
0,49	$1 + \frac{1}{10,91}$	$1 + \frac{1}{0,6}$

So k always larger than n , but the ratio $\frac{k}{n}$ decreasing with n . That $\frac{B}{C} - \frac{1}{n-1}$ or $\frac{1}{k-1} - \frac{1}{n-1}$ must always be negative for the case that $\frac{dp}{dx} = 0$ passes through the top of $\frac{d^2\psi}{dx^2} = 0$, appears when we express the value of $\frac{B}{C} - \frac{1}{n-1}$ in x_g . This value is:

$$\frac{B}{C} - \frac{1}{n-1} = \frac{x_g(3x_g-1)}{1-2x_g} - \frac{2}{n-1}$$

or

$$\frac{B}{C} - \frac{1}{n-1} = \frac{x_g(1-x_g)}{1-2x_g} \left\{ -1 + \sqrt[3]{\frac{2(1-2x_g)^2}{x_g(1-x_g)}} \right\}$$

The factor of $\frac{x_g(1-x_g)}{1-2x_g}$ is only $= 0$ for $x_g = \frac{1}{3}$ and negative for every value of x_g between $\frac{1}{2}$ and $\frac{1}{3}$, between which values it lies.

For all values of $T < T_g$ the section of the two surfaces has the shape of fig. 24a (Contribution V, p. 134). For $T = T_g$, $\frac{d^2\psi}{dx^2} = 0$ has contracted to a single point, and the line $\left(\frac{dp}{dx}\right)_{vT} = 0$ has the minimum volume exactly at that point.

If we take k still larger than was calculated above the section of the two surfaces will pass round the top, and there is again question of a maximum temperature, which, of course, lies then again below T_g . At this maximum temperature there is again contact between the two curves, but then the contact is such that $\left(\frac{d^2\psi}{dx^2}\right)_{vT} = 0$ lies entirely in the region where $\left(\frac{dp}{dx}\right)_{vT}$ is positive, except in the point of contact, where $\frac{dp}{dx} = 0$. The point of contact lies then on the branch of $\left(\frac{dp}{dx}\right)_{vT} = 0$, where $\frac{dv}{dx}$ is negative.

This, however, does not exhaust all possible cases for the intersection of the two surfaces. Some more remarks remain to be made. We first observe that if $\frac{da}{dx}$ is negative, there are no points of the intersection for the values of x for which this is the case. For such points $B + Cx$ is negative, which can only be the case for positive C if B is negative.

In the quadratic equation in $(v-b)$ the factor of $\frac{v-b}{\frac{db}{dx}}$ has become positive on account of $B + Cx$ being negative, and the third term $B - \frac{C}{n-1}$ is also positive, because $\frac{B - \frac{C}{n-1}}{B + Cx}$ has both its numerator and its denominator negative. So no positive value of $v-b$ can satisfy this equation. In the second place we observe that for the value of x for which $\frac{da}{dv} = 0$, the value of $v-b$ is infinite, and the value of T

equal to 0. The projection of the section of the two surfaces on the v, x -plane is then a curve which starts at $x = 1$ and $v = b_2$, and has an asymptote for the value of x for which $\frac{da}{dx} = 0$. The T, x -projection of the section is then a line which has a value for T equal to zero at $x = 1$ and $x = -\frac{B}{C}$, and which has a maximum T somewhere between these two values of x . It is clear that at this value of T , at which the curves $\left(\frac{d^2\psi}{dx^2}\right)_{vT} = 0$ and $\left(\frac{dp}{dx}\right)_{vT} = 0$ touch, the contact takes place as in the case discussed last, and that the top of $\frac{d^2\psi}{dx^2} = 0$ lies in the region where $\frac{dp}{dx}$ is positive. And in the third place we draw attention to the special case that $B = 0$, or $a_{12} = a_1$ or $k = \infty$. Then the value of x , for which $\frac{da}{dx} = 0$, is itself equal to 0. The equation for the determination of $v-b$ of the section of the two surfaces simplifies then to:

$$\frac{(x-b)^2}{\left(\frac{db}{dx}\right)^2} - (1-x)\frac{v-b}{\frac{db}{dx}} - \frac{1-x}{n-1} = 0$$

or

$$\frac{v-b}{\frac{db}{dx}} = \frac{1-x}{2} + \sqrt{\frac{(1-x)^2}{4} + \frac{1-x}{n-1}}$$

This represents a branch of a hyperbola which passes through the point $x = 1$ and $v = b_2$ and cuts the axis $x = 0$ for a value of:

$$v = b_1 + \left(\frac{b_2 - b_1}{2}\right) \left\{ 1 + \sqrt{1 + \frac{4}{n-1}} \right\}.$$

The quantity $k = \frac{a_2 - a_{12}}{a_{12} - a_1}$, on which it depends in so high a degree whether the considered surfaces intersect or not, and the way in which they intersect, is, for the same value of a_2 and a_1 , entirely determined by the value which we must assign to a_{12} . If a_{12} decreases from a_2 to a_1 , k increases from 0 to ∞ . For $a_{12} = \sqrt{a_1 a_2}$ it has the value $\sqrt{\frac{a_2}{a_1}}$ and then one of the transition cases $k = n$ would be $\frac{a_2}{n^2} = a_1$, or the critical pressure of the two components

has the same value. But until the relation between a_1 , a_2 and $a_{1,2}$ is known, such a simple rule cannot be considered as valid.

The calculation of the temperatures at which the two curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{dp}{dx} = 0$ are in contact cannot be performed on account of the very intricate forms to which this problem leads. For this purpose we might solve the value of $v-b$ from the quadratic form of page 201, which is then a function of x , and substitute then the value of v , either in $\frac{dp}{dx} = 0$, or in $\frac{d^2\psi}{dx^2} = 0$. We have then a formula in which T is expressed in the values of x of the points of intersection of the two curves. If we seek the maximum value of T by differentiating with respect to x at $T = \text{constant}$, we find a relation in x , from which the x of the points of contact would have to be calculated, and the value of T_{max} or T_{min} by substitution of this value of x . But even in the special case of $\frac{B}{C} = \frac{1}{n-1}$, or $k = n$, in

which $v - b = \frac{db}{dx} \frac{x(1-x)}{1 + \frac{x}{n-1}}$, this calculation leads to a form in which

x rises to the third degree. In all other cases the equation is much more intricate. The value of x , v and T for the maximum and minimum temperature might of course also be calculated by the aid of the three equations:

$$\frac{d^2\psi}{dx^2} = 0, \quad \frac{dp}{dx} = 0 \quad \text{and} \quad -\frac{d^3\psi}{dx^3} \frac{d^2p}{dx dv} = \left(\frac{d^2p}{dx^2}\right)^2,$$

which last equation expresses that the two curves touch. As $\frac{d^2p}{dv dx}$ is certainly negative in the points of the line $\frac{dp}{dx} = 0$, $\frac{d^3\psi}{dx^3}$ must certainly be positive for the contact, which had already been represented in the figures 24 of these contributions.

Physics. — “*Anomalous refraction phenomena investigated with the Spectroheliograph.*” By Prof. W. H. JULIUS.

According to the current interpretation of spectroheliograph results, *dark* flocculi indicate regions on the sun, where the special gas, a line of which is used, exists in such conditions of density and temperature, that it strongly absorbs the light coming from deeper layers, whereas *bright* flocculi show us regions where, in consequence of higher temperature or chemical or electrical causes, the radiation of the gas exceeds its absorbing effect.

A few years ago I proposed an entirely different explanation of the same phenomena¹). An attempt was made to account for the peculiar distribution of the light in photographs, secured with the spectroheliograph, by simply considering the anomalous refraction which waves from the vicinity of the absorption lines must suffer when passing through an absorbing medium, the density of which is not perfectly uniform.

If it proves possible to explain the observed facts on this basis, we shall be able to dispense with the assumption of any very marked differences as to the absorbing and emitting conditions of a certain gas or vapour in contiguous regions on the sun. Moreover, we then *might* assume the constituents of the solar atmosphere to be thoroughly mixed, their proportions in the mixture only varying with the distance from the sun's centre.

That our interpretation does not presuppose the separate existence of cloud-like masses of calcium or iron vapour or of hydrogen, simplifies the conception of the solar body, and therefore looks like an advantage; but even if one were compelled, by other considerations, still to believe in the real existence of such separate luminous or dark accumulations of certain substances, it would nevertheless be necessary to consider the effect, which anomalous dispersion of light in those masses must have on the appearances revealed by the spectroheliograph.

Among the advantages I derived from a visit to the Mount Wilson Solar Observatory, in August 1907, was the opportunity of using the 5 foot spectroheliograph²) for some experiments on anomalous refraction.

It was expected that when light, coming from a source with a continuous spectrum, traverses a space in which sodium vapour is

¹) Proc. Roy. Acad. Amsterdam VII, p. 140, (1904).

²) HALE and ELLERMAN. “The five-foot spectroheliograph of the Solar Observatory.” Contributions from the Solar Observatory Mount Wilson, California, N^o. 7.

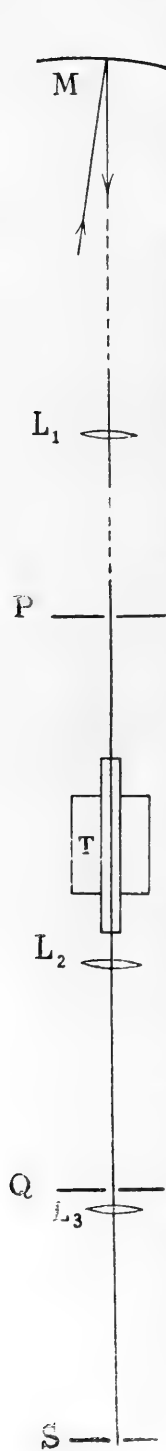


Fig. 1.

unequally distributed, particulars concerning the distribution would be revealed by the spectroheliograph through the *refracting* power of the vapour, rather than through its absorbing and emitting power. This expectation could be put to the test.

As an equipment for the study of anomalous dispersion phenomena in sodium vapour, exactly similar to the one described in my paper on "Arbitrary distribution of light in dispersion bands"¹⁾, had already been procured for the solar observatory by Professor HALE, the experiments were readily made, thanks to the laboratory facilities available on the mountain.

The apparatus consists of a wide nickel tube, 60 c.m. long, the middle part of which is placed in an electric furnace, while the projecting ends are cooled by jackets with flowing water. The tube contains a few grammes of sodium and is permanently connected to a Geryk-pump to remove the air and the gases which escape from the sodium during the first stages of the heating process. An arrangement is provided for, by which density gradients of various known directions and arbitrary magnitude may be produced in the sodium vapour.

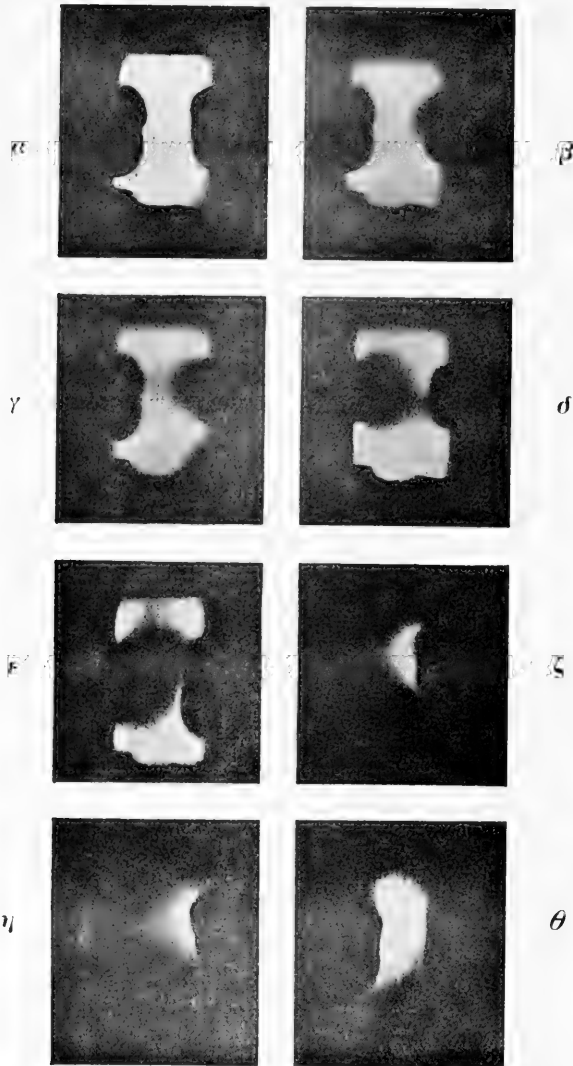
Sunlight coming from the 60 feet mirror *M* (fig. 1) of the Snow telescope²⁾ passes through the tube *T* on its way to the slit *S* of the spectroheliograph. The distance between *T* and *S* is about 560 c.m. A lens *L*₁ gives an image of the sun near the middle of the tube *T*. *P* is a diaphragm with an adjustable slit, of which the lens *L*₂ projects an image in the plane of the diaphragm *Q*. Just behind the latter is a lens *L*₃; in combination with *L*₂ this forms an image of a section of the tube in the plane of the slit *S* of the spectroheliograph. In this image (fig. 2) the rectangular windows of the caps of the tube will of course come out with somewhat blurred edges, as only a section lying somewhere *between* the caps would show sharp. In *A* and *B* are projected the narrow nickel tubes³⁾,

¹⁾ Proc. Roy. Acad. Amsterdam, IX, p. 343. (1906).

²⁾ Described in: Contributions from the Solar Observatory Mt. Wilson, Cal., Nos. 2 and 4.

³⁾ See description in: Proc. Roy. Acad. Amsterdam, IX, p. 345.

W. H. JULIUS. "Anomalous refraction phenomena investigated with the spectroheliograph."



of which, for producing the required density gradients, the temperature may be varied at pleasure by forcing an electric current or an air current through them.

Cooling one of the tubes by an air current causes sodium vapour to condense on it; so, in course of time, drops of molten metal will hang from the tubes and fall off again.

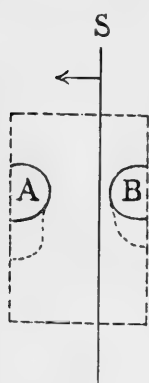


Fig. 2.

When a photograph is made, the first slit S of the spectroheliograph moves across the image in the direction of the arrow (fig. 2), and at the same time the second slit moves across the photographic plate.

Let us suppose the openings in P and Q (fig. 1) to be so adjusted, that the image of the slit in P exactly coincides with the slit in Q . Then all the light which passes through P and traverses the vapour along straight lines, is transmitted by Q and therefore contributes to the intensity of the image of the tube-section.

Waves however that deviate so much in the sodium vapour as to be intercepted by the screen Q , will be absent from the spectrum of the transmitted light.

If the furnace is slowly heated to 380° or 390° , the density of the vapour is pretty uniform in the middle part of the wide tube and falls off towards the ends; but as the direction of these density gradients nearly coincides with that of the beam of sun-light, even the waves subject to anomalous dispersion will hardly deviate from the straight path. The D -lines in the spectroheliograph retain about their normal appearance. If now we blow air through the tube B , density gradients are produced all around it in directions perpendicular to the axis of that tube. The D -lines no longer show the same appearance throughout the field. In the spectrum of those parts of the field where perceptible gradients occur, the D -lines now appear winged; they are indeed enveloped in *dispersion bands*. As the width of these bands depends on the magnitude of the gradient, it will, in our case, vary along the lines and reach a maximum at the place in the spectrum which corresponds to the plane passing through the axes of the tubes A and B . And with increasing distance between S and B (fig. 2) the width of the bands will diminish.

Let us consider the monochromatic images of the tube-section produced by the spectroheliograph if the camera slit is set at different distances from the D -lines.

With the camera slit at $\lambda 5850$, outside the region of the dispersion band of D , the illumination of the field is uniform (see the Plate, a);

nothing is visible of the density gradients existing round the cooled tube B , because light of this wave-length travels along straight lines through the vapour.

Proceeding to $\lambda 5870$, we are still at such a distance from D_2 , that the value of $\frac{1-n}{\Delta} = R$ (n representing the index of refraction, Δ the density of the vapour) is moderate. Steep gradients of the density are required to make the rays deviate sufficiently for missing the slit in Q , and such gradients are only to be found very near the surface of the tube B . We therefore obtain the image β , in which B appears surrounded by a narrow dark region.

The third photograph, γ , has been made with $\lambda 5877$. For these waves the expression $\frac{1-n}{\Delta}$ is greater than for $\lambda 5870$, so that smaller values of the gradient suffice to give to the rays a perceptible incurvation. The result is a broader dark region all round B ¹⁾.

The photographs δ and ε have been secured with the camera slit on $\lambda 5881$ and $\lambda 5885$ respectively. This time the tube A has been cooled instead of B . We see the dark "aureole" grow as the wave-length we are using approaches $\lambda_{D_2} = 5890$. Getting nearer still, the whole field would finally become dark.

Similar results are obtained if we approach D_1 from the side of the *greater* wave-lengths, thus using waves for which $\frac{n-1}{\Delta}$ has increasing values.

By a slight change in the arrangement of our experiment we may obtain the opposite effect, to wit, that merely rays, suffering anomalous refraction, do enter the spectroheliograph, whereas the normally refracted light is prevented from reaching the slit. We have only to open the slit in P very wide, and to put a vertical bar (a match for instance) in the middle of it, the image of which now falls exactly on the slit in Q . Under these circumstances light, issuing from the divided opening in P , can only be transmitted by Q if it has been deflected in the vapour.

In this way the photographs ζ , η and θ were obtained, the second slit being set on $\lambda 5884$, $\lambda 5886$, $\lambda 5888$ respectively. If there had been no density gradients, the whole field would have shown dark; the *bright* regions, however, now prove the existence of the gradients. When taking ζ and η , the tube B , and when taking θ , the tube A was cooled.

¹⁾ In this image the lower right corner was cut off by a rubber tube accidentally crossing the path of the beam.

The following general statement is borne out by these experiments.

If an illuminated absorbing vapour is investigated by means of the spectroheliograph, and the camera-slit of the instrument is set *on the edge* of a dispersion band, marked irregularities in the brightness of the field will only appear at those places in the image which correspond to regions with *large* density gradients in the vapour. Setting the slit *nearer to the middle* of the dispersion band, we shall get evidence, in the image, also of regions with *smaller* gradients, a.s.o. Particulars regarding the distribution of a vapour are thus clearly shown by the spectroheliograph through anomalous refraction, even in cases, where the absorbing or emitting power of that medium would have failed to reveal its structure.

The bearing of these inferences on astrophysical phenomena has now to be considered a little more closely.

Suppose we have a large mass of absorbing vapour of such average density, that, if it were uniform, its absorption lines would appear rather narrow; and of such temperature and condition of luminescence that its emission lines are very faint. As soon as the density of this mass becomes irregular, some parts of it may give rise, when traversed by light from another source, to the appearance of dark or bright dispersion bands, greatly exceeding in width and strength its absorption or emission lines.

It is therefore *possible*, that anomalous refraction plays a very essential part in the production of those phenomena which the student of astrophysics observes with his spectroscope or spectroheliograph; we must inquire how far this is also *probable*.

One might be inclined to object, for instance, that in our experiment the use of a narrow and sharply limited source of light, placed at a fair distance behind the vapour, seemed to be a necessary condition for obtaining any marked dispersion effects, and that in the sun similar circumstances are very unlikely to prevail. Indeed, the bulk of the sun — whatever the nature of the photosphere may be — is a large incandescent mass, closely surrounded by the absorbing vapours, so that the “source of light”, if considered from a point of the chromosphere, subtends a solid angle of nearly 2π . The reversing layer and the chromosphere have sometimes been compared to a thin, transparent layer of selectively absorbing varnish, covering a luminous (e.g. phosphorescent) globe: the photosphere. It seems very improbable that refraction in density gradients of such a transparent envelope should be able to disturb to any perceptible degree the uniform brightness of that globe.

The comparison, however, is entirely misleading, because, so far, an essential relation between absolute size and density gradients is overlooked in it. But if carried through properly, it will lead us to the opposite conclusion, namely that refraction in the solar atmosphere must alter the distribution of the light on the disk entirely.

If we wish to form an image, on a reduced scale, of the sun considered as a refracting body, we have to reduce the radii of curvature of the rays in the same proportion as we do the diameter, for instance 10^{10} times (so as to make the diameter of the photosphere 14 cm.). By the general equation¹⁾

$$\frac{d\Delta}{ds} = \frac{1}{R\varrho} \quad (1)$$

we know that, for a given value of the refraction constant R , the radius of curvature ϱ of a beam of light is in reverse proportion to the density gradient $\frac{d\Delta}{ds}$ in the direction toward the centre of curvature. In our image, therefore, the density gradients have to be taken 10^{10} times as great as they are in the sun.

Let us suppose that at a certain level in the solar atmosphere irregular density gradients occur, which are of the same order of magnitude as the radial (vertical) density gradient in our earth's atmosphere, viz. 16×10^{10} ²⁾. At the corresponding points in our image we then have to put $\frac{d\Delta}{ds} = 16$. If the layer of "varnish"

were really traversed by many density gradients of this order of magnitude, it would be very different from ordinary transparent varnish, and certainly be able to disturb the uniform brightness of the background, like a layer of glass beads or swollen sago grains. Even normally refracted waves would perceptibly deviate in an envelope of this kind. For if in our equation (1) we put $\frac{n-1}{\Delta} = R = 0,5$ and $\frac{d\Delta}{ds} = 16$, we get $\varrho = 0.125$ cm., so that the average curvature of such rays is already sufficient for producing sensible changes in the divergence of beams on their way through a shell not thicker than 0.1 cm.

1) Proc. Roy. Acad. Amsterdam, IX, p. 352. (1906).

2) The frequent occurrence of density gradients nearly perpendicular to the radii of the sun is rendered more probable still, since increasing evidence has been obtained by Prof. HALE of the existence of solar vortices, in which the convection currents (especially in sun-spots) are sufficiently strong to produce magnetic splitting of absorption lines. (Cf. Nature, Vol. 78, p. 368—370, Aug. 1908).

Waves, suffering anomalous refraction, will of course be much more scattered by the same medium. Let us consider an absorbing substance which, at a certain level, occupies say only 1 percent of the solar atmosphere, taken as a perfect mixture. Its density gradients will then be only $\frac{1}{100}$ of those of the mixture. The refraction constant, on the other hand, for waves near one of its absorption lines, may attain values as high as 1000 or 2000. With $R = 1600$ (as actually observed in sodium vapour, Proc. Roy. Acad. Amst. IX, p. 353), our equation (1) becomes

$$\frac{1}{100} \frac{d\Delta}{ds} = \frac{1}{1600 \rho}.$$

In a level where, in our image, the irregular density gradients of the envelope were supposed to have an average value $\frac{d\Delta}{ds} = 16$, the equation gives

$$\rho = 0,004 \text{ cm.}$$

It is evident that under such circumstances rays may easily deviate 90 degrees and more in the thin shell of transparent matter covering our globe, and thus give rise to a very unequal distribution of the light in photographs of it, secured with the spectroheliograph.

This conclusion holds just as well with regard to the real sun. It follows directly from our *only* assumption, that in some level of the sun irregular density gradients exist, comparable in magnitude with the vertical gradient in the earth's atmosphere. At lower levels, greater gradients, at higher levels, smaller gradients may be expected to prevail. As the validity of this assumption can hardly be doubted, we may infer that the existence of some important influence of anomalous dispersion on astrophysical phenomena is not merely possible, but *exceedingly probable*, in spite of the absence of narrow slits as sources of light.

Although we are free to admit that the phenomena, observed with the spectroheliograph on the solar disk, are perhaps in part due to selective radiation, dependent on various conditions of temperature or luminescence, we may nevertheless inquire into some consequences to which one is led if only the effects of refraction in a mixture of vapours are considered.

The composition of the solar atmosphere cannot be the same at all levels. As we get lower down, the percentage of heavier molecules is likely to increase; but we should not presume too much

as to the order in which the elements will come into evidence, on account of possible condensation, and because the pressure of radiation counteracts gravitation to a degree that depends on the size of the particles, and, therefore, on numerous unknown conditions prevailing in the sun.

Yet for each element a certain level must exist, in which its percentage in the mixture is a maximum. Accordingly, the refracting properties of successive layers will be governed by different elements. A photograph, made with the spectroheliograph in a hydrogen line, shows a structure which, of course, depends on the distribution of all the hydrogen present in successive layers, but is chiefly determined by the density gradients in a rather high level; whereas a photograph, made with an equally strong iron-line, reveals more especially the structure of lower regions. This explains the difference in character between iron- and hydrogen plates.

It must be possible, on the other hand, to obtain almost identical photographs with different lines, provided they belong either to the same element, or to elements that are most in evidence at about the same level in the sun; but then another condition has also to be fulfilled, viz. that the camera-slit transmits rays of the same

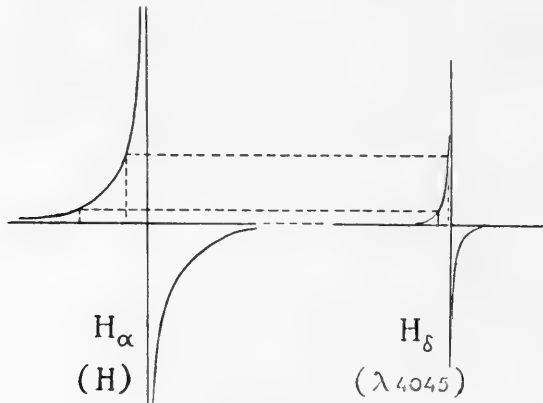


Fig. 3.

refrangibility in both cases. If for instance Fig. 3 represents the dispersion curve near H_z and near H_δ , the width and the position of the camera-slit ought to be so chosen, as to let in only waves corresponding to parts of the curve, enclosed between equal ordinates in the two dispersion bands ¹⁾.

¹⁾ Waves, lying more or less symmetrically on either side of an absorption line, and answering the relation $n-1 = 1-n'$ between the indices of refraction n and n' of the medium for them, must give nearly the same spectroheliograph results on the greater part of the disk. This follows from a discussion of the various possi-

Recently it has been found by Prof. HALE that, while the H_{β} -, H_{γ} - and H_{δ} -lines give very similar results, photographs with the much stronger line H_{α} are widely different in some respects¹⁾. Bright flocculi appear on these plates at points where no corresponding objects are shown by H_{δ} . Moreover, the dark H_{α} -flocculi, while showing a general agreement in position and form with those of H_{δ} , are stronger and more extensive. In some instances, however, small areas appear dark in H_{δ} which are absent or fainter in H_{α} .

Such differences are of the same character as those observed between photographs made with the slit in the broad calcium-bands H or K at various distances from the central line. They may find a corresponding explanation if we assume that the rays, used in the H_{α} photographs, were on the average refracted to a higher degree than those, used in the H_{δ} -photographs, but both by the same system of density gradients. It is not improbable, therefore, that in the wings of H_{α} waves may be selected so as to give spectroheliograph results, closely resembling H_{δ} -plates.

That also lines of *different* elements may give very similar results with the spectroheliograph, is exemplified by the case of calcium and iron. Among the beautiful collection of photographs secured on Mount Wilson I saw several iron-(λ 4045)-plates rather closely resembling certain calcium-(H_1)-plates of the same daily series. As the atomic weights of calcium and iron are not so very different, and their levels of maximum density therefore probably not far apart, the refraction caused by these elements may bring out the density gradients of nearly the same layer of the solar atmosphere. It will do so by showing a similar distribution of the light in the two photographs — provided that rays of the same refrangibility are used in both cases. And this condition may be fulfilled by setting the camera slit on corresponding regions of the spectrum, in the sense as illustrated by Fig. 3, if we imagine it now to bear on the calcium-(H)-line and the iron-(λ 4045)-line.

With a calcium- and a hydrogen-line such similarity could not be found.

Far more evidence will of course be required before we shall be able to decide whether or not anomalous dispersion is the principal agent in determining the flocculent appearance of the solar disk.

bilities regarding the relative position of density gradients and source of light. Consequently a H_{δ} -plate, obtained with the camera-slit centrally, so as to embrace the whole width of that rather narrow dispersion band, will scarcely differ, at first sight, from a photograph made with only one of the wings.

²⁾ HALE, "Solar vortices", Contrib. from the Mt. Wilson Solar Obs. No. 26.

Plates secured with many lines of various elements will have to be compared. The mighty 30-foot spectroheliograph of the "tower telescope" of Mount Wilson is excellently adapted to work of this kind, not only on account of its great dispersion permitting the use of finer lines, but chiefly because it is provided with two camera slits, so that perfectly simultaneous photographs with different lines may be secured. By this arrangement, really comparable monochromatic pictures of the sun are obtained, since the otherwise confusing influence of the variable refraction in our atmosphere is thus rendered harmless.

I feel greatly obliged to Prof. GEORGE E. HALE for having procured for me the opportunity of making an investigation at the Mount Wilson Solar Observatory, but more still for his keen and stimulating interest in the problems, suggested by the application of the principle of anomalous refraction in astrophysics. I am also very much indebted to the kindness of Mr. F. ELLERMAN, Mr. W. S. ADAMS and Dr. CH. M. OLMSTED for valuable information and assistance in connection with the inquiry here reported upon.

Physics. — "*The ZEEMAN-Effect of the strong lines of the violet spark spectrum of iron in the region λ 2380— λ 4416.*" By MRS. H. B. VAN BILDERBEEK-VAN MEURS. (Communicated by Prof. P. ZEEMAN).

The concave ROWLAND grating used in the experiments here communicated has 14438 lines per inch, a width of 8 c.m., and a radius of curvature of 304.96 c.m. The grating is mounted according to RUNGE and PASCHEN's method.

The spark passed between the iron poles of the magnet in the direction of the line of force. It was originated by the discharge of the secondary coil of a RUHMKORFF, a self-induction and condenser being placed in parallel.

Further details will be given in my thesis for the doctorate.

The time of exposure varies from 30 to 120 minutes.

In order to determine the field strength I made simultaneous exposures of the iron and zinc spectra. The amount of separation of the zinc line 4680.33 was compared with the result of the measurements of COTTON and WEISS (Journal de Physique, June 1908), the strength of field being supposed proportional to the amount of separation.

λ	I	$\frac{\delta\lambda}{\text{vibr. } \perp \text{ field}}$	$\frac{\delta\lambda}{\text{vibr. } // \text{ field}}$	$\frac{\delta\lambda}{H\lambda^2} 10^{13}$ vibr. \perp field	$\frac{\delta\lambda}{H\lambda^2} 10^{13}$ vibr. $//$ field
2382.17	10	0.214		11.80	
2395.74	4	0.206		11.23	
2562.65	5	0.238		11.34	
2585.98	10	0.292		13.66	
2598.46	8	0.310		14.36	
2599.50	20	0.334		15.46	
2607.17	10	0.315		14.50	
2611.99	10	0.335		15.36	
2617.70	6	0.361		16.48	
2625.70	4	0.324		14.70	
2628.39	8	0.229		10.37	
2631.12	4	0.299		13.51	
2631.44	3	0.289		13.06	
2727.64	6	0.379		15.94	
2739.63	15	0.327		13.63	
2743.28	8	prob. unaffected			
2746.60	10	0.222		9.206	
2747.08	8	0.306		12.69	
2749.41	20	0.272		11.26	
2753.40	5	0.245		10.11	
2755.80	15	0.278		11.45	
2767.60	5	0.418		17.07	
2767.03	5	0.220		11.37	
2994.58	3	0.439		15.31	
3001.09	2	0.397		13.79	
3002.82	3	0.388		13.45	
3008.26	2	0.413		14.28	
3020.80	3	0.412		14.13	
3037.51	3	0.433		14.68	
3047.72	3	0.440		14.82	
3057.57	3	0.345		11.54	
3059.20	3	0.446		14.91	
3227.91	5	0.354		10.63	
3440.79	4	0.434		11.47	
3466.01	3	0.759	0.389	19.77	10.13
3475.60	3	0.625	probably div.	16.19	
3490.76	4	0.574	" "	14.74	
3497.99	3	0.772	" "	19.74	
3513.98	3	0.555		14.06	
3555.08	4	0.516		12.77	
3558.69	4	diffuse			
3565.53	5	0.349		8.589	
3570.29	10	0.420		10.31	
3581.34	10	0.460		11.22	
3585.48	3	0.446	0.387	10.85	9.418
3587.11	3	diffuse	0.489		11.89
3606.85	4	0.429		10.32	
3609.01	6	0.183		4.395	
3618.91	6	0.327		7.811	
3631.62	6	0.368		8.729	
3647.99	6	0.391		9.192	
3649.62	3	0.493		11.58	
3680.09	3	0.574	probably div.	13.26	
3687.61	4	0.626		14.40	
3705.72	4	0.565	0.262	12.87	5.969
3709.40	4	0.632		14.37	
3720.09	10	0.496		11.21	

λ	I	$\frac{d\lambda}{\text{vibr. } \perp \text{ field}}$	$\frac{d\lambda}{\text{vibr. } // \text{ field}}$	$\frac{d\lambda}{H\lambda^2} 10^{13}$ vibr. \perp field	$\frac{d\lambda}{H\lambda^2} 10^{13}$ vibr. $//$ field
3722.71	4	0.558	0.392	12.60	8.849
3727.78	5	0.659		14.84	
3733.47	3	0.355 0.354	0.587	7.968 7.945	13.17
3735.00	10	0.592		13.28	
3737.28	7	0.459		10.28	
3745.70	5	0.474		10.57	
3748.40	4	0.276	perhaps divided	6.145	
3749.62	10	0.574		12.77	
3758.39	8	0.540		11.96	
3763.98	6	0.422		9.318	
3765.70	3	0.484		10.68	
3767.36	5	0	0	0	0
3795.14	5	0.692		15.03	
3799.70	5	0.662		14.34	
3805.48	3	0.386		8.339	
3813.12	4	0.414		8.908	
3816.00	10	0.495		10.63	
3820.61	10	0.529		11.34	
3821.57	5	0.694		14.84	
3826.08	8	0.494		10.56	
3828.00	7	0.451		9.629	
3834.41	6	0.431		9.170	
3840.61	4	0.313		6.426	
3850.19	4	0	0	0	0
3856.55	5	0.690		14.51	
3860.12	6	0.682		14.32	
3865.75	4	0.348 0.348	0.658	7.285 7.285	13.78
3872.70	4	0.594	0.473	12.39	9.866
3878.20	4	0.812		16.89	
3878.78	5	0.715		14.87	
3886.45	5	0.802		16.61	
3885.80	3	0.676		13.93	
3903.10	5	0.544	0.217	11.17	4.456
3920.41	4	0.634		12.90	
3923.08	4	0.694		14.11	
3928.09	4	0.705		14.29	
3930.47	4	0.715		14.48	
3969.43	5	0.758		15.05	
4005.41	6	0.787		15.35	
4045.99	15	0.618		11.81	
4063.78	10	0.544		10.31	
4071.90	8	0.351		6.623	
4181.92	4	0.700		12.52	
4199.27	5	0.577		10.24	
4212.21	6	0.617		10.93	
4236.12	4	0.982		17.12	
4250.19	6	0.537	0.404	9.296	6.994
4260.70	10	0.878		15.13	
4271.99	10	0.705		12.07	
4294.32	4	0.608		13.31	
4299.43	4	0.799		13.37	
4308.10	15	0.648		10.92	
4325.97	15	0.528		8.826	
4383.73	20	0.697		11.35	
4404.95	15	0.678		10.93	
4415.30	10	0.654		10.50	

The strengths of field used in all other exposures, could be determined by comparison of corresponding iron lines in the spectrum under review and in the standard iron-zinc spectrum.

The field strengths utilised were near 30000 Gauss. In the following table all separations are reduced to $H = 31965$ Gauss.

A calcite rhomb introduced between the spark and the focussing lens made it easy to get separate exposures of vibrations perpendicular to resp. parallel to the field. The plates used were Dr. SCHLEUSSNER's Spezial Rapid plates. They were developed with Edinol.

In the following table $\delta\lambda$ and λ are given in Å.U. The wavelengths and intensities are taken from EXNER and HASCHER's tables.

In the case of triplets and quartets $\delta\lambda$ indicates the difference of the wavelengths of the two outer components vibrating perpendicular or parallel to the lines of force. In the case of quintets for vibrations perpendicular to the lines of force the difference of wavelengths of the components towards red and violet to the central one are given. For vibrations parallel to the lines of force the data are given as in the case of triplets.

Probably some triplets can be subdivided further, but even an approximate knowledge of the magnetic separation of the iron lines has become recently of some value by HALE's important discovery concerning the spectrum of sun-spots¹⁾.

I hope to give in my thesis references to the literature of the subject.

Anatomy. — "*The nervous system of a white cat, deaf from its birth: A contribution to the knowledge of the secondary systems of the auditory nerve-fibres*". By Prof. C. WINKLER.

Through the kindness of Prof. ZWAARDEMAKER, speaker got in his possession the nervous system of a white blue-eyed cat, which during life, though most carefully observed, never reacted on acoustic stimuli, consequently deaf from its birth²⁾.

This nervous system had been slightly damaged in the removing,

¹⁾ GEORGE E. HALE. Solar Vortices and the ZEEMAN-Effect.

P. ZEEMAN. Solar Magnetic Fields and Spectrum Analysis. Nature. Vol. 78, p. 368 and 369, 1908.

²⁾ Prof. ZWAARDEMAKER writes on this subject the following:

"This white catt, born of a white mother with normal hearing (one albino-eye) was obviously deaf from its birth. At any rate it was kept under observation since birth, and never a single reaction on acoustic stimuli was obtained. Even

probably because the tentorium, ossified in these animals, had been drawn through the occipital pole of the hemispheres.

With the exception of this damaged portion it was possible to make a continue series of frontal sections, partly after the WEIGERT-PAL method, partly coloured by means of carmine, which could be compared with the existing series of frontal sections from brains of normal cats.

The first thing noticed was that the peripheral octavus-roots which were attached to the oblongata, although smaller than in the compared preparations, *had not suffered any change*. In accord with this fact no degenerations were found either in the lateral rootfibres upon the corpus restiforme, or in the rootfibres in the ventral nucleus of the VIIIth nerve, or in the deep medullated layers of the tuberculum acusticum (speaker exhibits the microphotograms demonstrating those rootfibres.)

Although these nuclei too are somewhat smaller than in the compared series, yet it is impossible *that the deafness of this cat should have been occasioned by a primary affection of the labyrinth*. For in that case the well-determined and distinctly confined atrophies would have been found in the systems of primary rootfibres, which are in all cases consequent to the removal of the labyrinth in newborn animals. (These atrophies are demonstrated by the speaker on preparations and microphotograms of brainsections taken from rabbits where the labyrinth had been removed shortly after birth).

Those atrophies however were not found in the brain of this cat. The more striking is the fact that a secondary system of fibres, the dorsal octavus-tract, the so-called stria acustica (v. MONAKOW)

“an express investigation with the continue note-series and with strong sound-stimuli gave only negative results.

“The statical organ on the contrary was proved to be perfectly normal. On the 7th of June 1908, shortly before death, this was carefully studied in my Laboratory.

“Climbing along the frame of a rotation-apparatus was done in the normal manner, likewise leaping from a chair. During rotation, when shut up in a blackened chest, with an aperture on the upperside in order to facilitate the observing of what is going on within, nystagmus of the head and of the eyes was shown in the usual way.

“On stopping the apparatus, a typical instance was observed of the well-known after-rotation, described once again by Mr. VAN ROSSEM (Sensations and reflexes, having their origin in the semi-circular canals. Diss. 1907, Utrecht).

“Upon the small experimentation-lift of W. MULDER, whilst seeing is excluded, all otolittic-reflexes are recognized, and nowise impaired.

“During life the animal mewed.”

in the deaf-born cat does not attain to $\frac{1}{4}$ of the compass that fascicle presents in the series taken for comparison.

The fibres originating in this fascicle and decussating in the raphe (the vigorous decussation of VON MONAKOW) are nearly all wanting. MONAKOW's decussation is represented barely by a few small fibres.

Likewise the fibres of HELD and their decussation are almost entirely wanting. On the other hand, the ventral secondary octavus-tract in the ventral layers of the corpus trapezoides is represented by a vigorous layer of fibres decussating in the raphe.

Together with the loss of MONAKOW's decussation the area at the dorsal and frontal top of the superior olivary bodies, where the fibres of MONAKOW's and HELD's crossings meet, is only represented by a few transverse sectioned fibres. It is wanting, and this deficiency in its turn is accompanied by a very important atrophy of the lateral lemniscus, more especially of its medial bundle of fibres. (The preparations and microphotograms illustrating this, are exhibited by the speaker).

Apparently nature did achieve in this cat, by some morbid process, a similar experiment as was made long ago by VON MONAKOW¹⁾, when he was the first who succeeded in isolating the dorsal octavus-tract by sectioning the lateral lemniscus.

For if the lateral lemniscus is sectioned, this so-called MONAKOW's decussation atrophies rather completely and the stria acustica is reduced to a small rest, whilst the large cells in the opposite tuberculum acusticum have nearly all disappeared and a certain number of cells are atrophied as well in the nucleus ventralis as in the portio interna corporis restiformis and in the nucleus of DEITERS. (The experimental loss and atrophy of those cells is demonstrated by means of preparations and microphotograms of brain-sections taken from rabbits, on which the section of the lemniscus had been performed directly after birth).

In the deaf-born cat almost all the large cells in the tuberculum acusticum have disappeared on both sides (and here — not in the loss of fibres — lies the cause of the slight decrease of the primary nuclei) whilst those in the dorsal portion of the nucleus ventralis, in the portio interna of the corpus restiforme and in the nucleus of DEITERS are partly atrophied.

This case therefore supplies a new argument in favour of the opinion *that the secondary system of true auditory nerve-fibres are to be sought for in the dorsal and intermediate octavus-tracts, in the*

¹⁾ C. VON MONAKOW. Striae acusticae und untere Schleife. Archiv für Psychiatrie, 1891. Bd. XXII. S. 1.

decussations of MONAKOW and HELD, and not in the ventral layers of the corpus trapezoides.

This opinion, put forward long ago by VON MONAKOW¹⁾ in opposition to the now generally accepted opinion of the school of FLECHSIG which presumes the course of the auditory fibres to be lying in the ventral systems of the corpus trapezoides, has been upheld by the speaker also once before.²⁾

The preparations from the deaf-born cat moreover enable us to find an answer to the question how this remarkable degeneration may be occasioned by a pathological process.

As is well-known, the roof of the 4th ventricle expands laterally into a so-called recessus lateralis, by which passes the tela chorioidea and consequently this latter is lying free at the ventral border of the oblongata.

At the entrance of this recessus, medial from the tuberculum acusticum (which forms the medial boundary of the recessus), the stria acustica is situated directly under the ependyme of the ventricle free at the surface.

Each hydrops ventriculi, tending towards dilatation of the recessus lateralis, becomes a danger for its surroundings, which may be oppressed either from the recessus lateralis as from the ventricle. It threatens to destroy successively first the stria acustica, next the tuberculum acusticum, and only after this latter the lateral root fibres become exposed. Now hydrops ventriculi may be caused by many different morbid processes, both of meningitis, ascending along the tela, and of encephalitis, complicated with ependymitis.

Now in this deaf-born cat we find hydrops ventriculi with a very important distention of the recessus lateralis, the tela chorioidea is thickened, with neo-formation of bloodvessels. The distention of the ventricle and that of its recessus undermined the lateral wall of the oblongata and the stria was pinched off. (This distention is demonstrated by the speaker on preparations and microphotograms).

Similar dilatations of the recessus with the tumefaction of the tela accompanying them, were found also in the IVth ventricle of deaf-and-dumb persons, together with atrophy of the stria acustica. The lateral root-fibres however were not always intact in such cases. They were sometimes destroyed, sometimes not. These facts will soon be published by Mr. A. BROUWER in his dissertation.

¹⁾ MONAKOW, l. c.

²⁾ C. WINKLER. The central course of the N. Octavus. Proceedings of the Royal Acad. of Sciences, 1907.

In our deafborn cat the hydrops ventriculi is nevertheless secondary to a morbid process situated elsewhere.

For in the left hemisphere are found the residua of a process of encephalitis having occurred long ago, in casu before birth.

This focus is situated in the left corona radiata and in the radiation of the corpus callosum. The cortex remains uninjured. Loss of fibres, tumefaction of glia-elements, formation of cavities and neo-formation of vessels mark the place where the focus is found.

Frontalward its boundary nearly coincides with the place where the gyrus lateralis divides into a gyrus ecto- and ento-lateralis. Thence it expands below the gyri supra- and ecto-sylvii mediales, caudalward not passing beyond the fissura ecto-sylvia posterior. There is a secondary atrophy of the medullated radiations of the following convolutions: the gyrus splenialis, supra-splenialis, ecto-lateralis, supra-sylvius medialis and ecto-sylvius medialis and in the lateral portion of the gyrus ecto-sylvius posterior. (Speaker demonstrates the position of this focus with the aid of drawings, preparations and micro-photograms).

This morbid process has entailed consequences.

1. The hydrocephalus internus mentioned before, which has distended the lateral ventricles, the third ventricle, the aquaeductus and the fourth ventricle, in the latter mere especially the recessus lateralis.

2. The macroscopically visible atrophy of the radiations towards the aforesaid convolutions and in the fibres of the corpus callosum.

3. The atrophy of cells, more intensive in the before-mentioned convolutions, though also very evident in other convolutions of the left hemisphere and likewise in the right hemisphere.

A loss of cells does not exist in the anterior convolutions, it begins far behind the zone where the pyramides of BETZ are found. The posterior pole was too much damaged to allow of any examination. But in the medial portions of the brain the degeneration is the following:

The loss and atrophy of cells is localized in the medial layers of cells of the cortex. The first layer of granular cells and that of the small pyramides are only slightly damaged, but the 4th stratum or interior granular layer and the 5th so-called sub-granular layer of the pyramides have lost all or a great number of the cells, the 6th or polymorphous layer of cells being again intact.

4. A macroscopically visible atrophy of the ventral nucleus of the left thalamus opticus, which has almost entirely disappeared at its frontal end and has lost cells as well as fibres.

5. A very slight atrophy in the most caudal part of the left

corpus geniculatum mediale, the more remarkable because therein many cells are lost, only there, were the brachium conjunctivum from the ganglion quadrigeminum posticum enters in the corpus mediale. At the same time the atrophy in the left brachium conjunctivum is more important than that on the right side. The preponderance of the atrophy in the left brachium, in accordance with the atrophy of the lateral lemniscus described before, is considered by the speaker as being occasioned by the encephalitic process. This focus was not situated (or only to a very small extent) in the temporal radiation of the corona radiata. It is not followed by an intense atrophy in the homolateral corpus geniculatum mediale, and therefore, cannot in itself be held answerable for the auditory defect of the animal.

This deaf-born white cat with the blue eyes consequently may not be considered to be a deaf variety of the genus cat. It is a pathological product. An encephalitis, probably during the intra-uterine life, has destroyed a part of the left hemisphere (not the so-called auditory radiation) and occasioned a hydrocephalus internus. Its pressure became a danger to all the systems at the surface of the ventricles. More especially those systems were endangered that were threatened from both sides by compression according to their position on the border of the recessus lateralis. The stria acustica was destroyed in that way.

Botany. — “On the investigations of Mr. A. H. BLAAUW on the relation between the intensity of light and the length of illumination in the phototropic curvatures in seedlings of *Avena sativa*.” By Prof. F. A. F. C. WENT.

Some years ago WIESNER¹⁾ attempted to ascertain, what is the minimum intensity of light to which various plants still react phototropically. He found; for instance, that with the epicotyl of *Pisum sativum* and the hypocotyl of *Lepidium sativum* the limit of sensitiveness is not yet reached at 0.054 normal candle power. (WIESNER expresses it in a unit which is equal to 6.5 Spermaceti candles). For the epicotyl of *Phaseolus multiflorus* the limit is exactly at 0.054 normal candle power. While in this case, the author does not mention the duration of the experiments, he states for the epicotyl of

¹⁾ J. WIESNER. Die heliotropischen Erscheinungen im Pflanzenreiche. Wien 1878. p. 178—180.

Vicia sativa, that, at an intensity of 0.054 N.C., the curvature began to appear after 3 hours and 45 minutes, whereas the same organ in *Vicia Faba*, with light of the same strength, did not show any curvature even after 48 hours. In none of these cases, therefore, has an attempt been made to find the minimum period, during which light of a given intensity must act on a plant in order to produce a phototropic curvature. Later FIGDOR¹⁾ carried out similar experiments; here only his conclusion can be mentioned, that the inferior limit of phototropic sensitiveness is below 0.0003262 normal candle power for seedlings of *Lepidium sativum*, *Amarantus melancholicus ruber*, *Papaver paeoniflorum* and *Lunaria biennis*.

CZAPEK²⁾ on the other hand has been engaged on a determination of the presentation-time; by this he means the minimum period of unilateral illumination, required for the subsequent production of a phototropic curvature. For seedlings of *Phalaris* and of *Avena* this period is stated by him to be about 7 minutes, although he furnishes no data as to the intensity of the light employed. Presumably the author did not perceive the necessity of such data, because his investigation was almost wholly concerned with geotropism, where the idea of presentation-time, without further specification, has a pretty definite meaning, because we are concerned with the constant force of gravity.

The question, whether there is a connexion between this presentation-time and the intensity of the light, was however close at hand. In his further investigation, on the perception of phototropic stimuli, Mr. A. H. BLAAUW has also taken up this question in my laboratory; he has arrived at some very striking results, about which I wish to make this brief preliminary communication.

The experiments were performed with etiolated seedlings of *Avena sativa*, the coleoptile of which is extremely sensitive to light stimuli, as is well known since the investigations of DARWIN and of ROTHERT.

For the weaker intensities an Auer von Welsbach burner (incandescent gas light) was used; it was kept very constant by means of a gas-pressure regulator. By placing the objects at varying distances from the lamp, and, where necessary, by screening the light through smoked glass, and further, by letting the light fall on a plate of opalescent glass with a diaphragm, which in its turn acted as source

¹⁾ W. FIGDOR. Versuche über heliotropische Empfindlichkeit der Pflanzen. Sitzber. d. Math. Naturw. Classe d. K. Akademie der Wissensch. Wien. Bd. CIII. Abth. I 1893, p. 45.

²⁾ F. CZAPEK. Weitere Beiträge zur Kenntniss der geotropischen Reizbewegungen. Jahrbücher für wissenschaftliche Botanik. Bd. XXXII. 1898. p. 185.

of light, all possible intensities were obtainable, from 100 Hefner candles downwards. The intensity was measured by means of a WEBER photometer. The gaslamp was outside the room containing the experimental plants, so that the latter were protected against any harmful effect of coal-gas.

For greater light intensities the electric arc-lamp of a lecture lantern was used, and by concentrating its light through lenses, strengths up to 48000 Hefner candles were obtainable.

The period of illumination varied from 13 hours to 0.001 second; the very short periods were obtained by means of a photographic instantaneous shutter with slit.

The plants were now placed at various distances from the source of light; they were illuminated for a given time and were then left in the dark and were examined for phototropic curvature after about 2 hours. When the distance and time had been properly chosen, a well-marked limit was found to occur, so that below a certain strength of light no curvature occurred, whereas above that strength all or nearly all the seedlings were bent towards the light. It may be said, therefore, that with a given exposure-time, a certain minimum intensity of light is required for perception, or, more correctly, for the production of a reaction, since of the actual perception of a light stimulus we know nothing.

It was already a striking result, that while, as stated above, the presentation time was assumed to be 7 minutes, Mr. BLAAUW in his experiments still obtained a reaction when the exposure was diminished to 0.001 second, provided the light was very strong.

The results become still more important if expressed numerically, as in the following table. The first column gives the length of the exposure, the second the corresponding intensity of the light (in Hefner candles) which just sufficed for a phototropic reaction; the third column gives the product of these two magnitudes, the time being expressed in seconds, so that the product might be called candles-seconds. In other words, the third column indicates in every case, how much light should have been allowed to fall on the plant during one second, in order to give the same amount of light as in the experiment.

I (Exposure).	II (Intensity of light).	III (Candles-seconds).
13 hours	0,000439 H.C.	20,6
10 "	0,000609 "	21,9
6 "	0,000855 "	18,6
3 "	0,001769 "	19,1

I (Exposure).	II (Intensity of light).	III (Candles-seconds).
100 minutes	0,002706 H.C.	16,2
60 "	0,004773 "	17,2
30 "	0,01018 "	18,3
20 "	0,01640 "	19,7
15 "	0,0249 "	22,4
8 "	0,0498 "	23,9
4 "	0,0898 "	21,6
40 seconds	0,6156 "	24,8
25 "	1,0998 "	27,5
8 "	3,0281 "	24,2
4 "	5,456 "	21,8
2 "	8,453 "	16,9
1 "	18,94 "	18,9
2/5 "	45,05 "	18,0
2/25 "	308,7 "	24,7
1/25 "	511,4 "	20,5
1/55 "	1255 "	22,8
1/100 "	1902 "	19,0
1/400 "	7905 "	19,8
1/800 "	13094 "	16,4
1/1000 "	26520 "	26,5

It follows at once from columns I and II that with a shorter exposure the strength of the light has to be increased, in order to obtain a curvature. The calculated values in column III show, in addition, that the intensity of light is inversely proportional to the length of exposure, or, in other words, that a definite quantity of light, independent of the exposure-time, is required to produce a reaction. It is true that the values in column III are not identical, but they clearly oscillate about a mean. Perfect identity cannot be expected in experiments of this nature, when it is remembered that the limit between curvature and non-curvature cannot always be determined exactly; moreover the oats seedlings are of course subject to individual variations, which could only be eliminated by making for each determination a long series of experiments; finally external conditions of humidity, temperature, etc. could not be kept perfectly constant in the various experiments.

There was not much point in choosing exposures of less than 0.001 second, nor of more than 13 hours, since the results obtained show clearly that the essential condition for the production of a phototropic curvature is the supply of a definite quantity of radiant

energy; whether this quantity be supplied in a very short time, or only extremely slowly, is a matter of indifference. This result is therefore in complete agreement with PFEFFER's view (at least as far as luminous stimuli are concerned) that the action of a stimulus is to be regarded as a phenomenon of "Auslösung".

A similar critical value for the stimulus has also been observed for the human eye. It is certainly very difficult to compare human observations with reactions of plants under the influence of light, but the observations of BLOCH and CHARPENTIER nevertheless indicate a close analogy between the two sets of phenomena. This is most readily shown by quoting a paragraph from the latter author¹⁾:

"Nous avons vu le minimum perceptible varier pour des durées de l'excitation allant de $\frac{2}{1000}$ à $\frac{125}{1000}$ sec. Dans ces conditions le minimum perceptible varie toujours sensiblement en raison inverse de la durée de l'excitation. Si la lumière est intense, elle produira cet effet en moins de temps, si elle est faible, elle devra, par contre, durer davantage. Pour que la sensation se produise il faut que, sur une zone rétinienne donnée et dans un certain temps, il arrive pour ainsi dire *une masse constante de lumière*, peu importe que cette masse se distribue sur un grand ou sur un petit espace et qu'elle arrive vite ou lentement sur la rétine. C'est là un fait important, dont il conviendra de rechercher les analogies sur d'autres territoires sensoriels."

From observations, published by BACH²⁾ we may perhaps deduce, that something of the same nature holds good for geotropic curvatures as has been found by Mr. BLAAUW for phototropic ones. I hope that further investigations in my laboratory will bring certainty on this point.

Utrecht, September 1908.

E R R A T U M.

p. 62 l. 12 from the top: for *uniform* read *uniformly*

p. 183 l. 14 ,, ,, ,, after „*hydrogen line*” insert *C*

¹⁾ CHARPENTIER. Archives d'Ophthalmologie. X. 1890, p. 122—123.

²⁾ H. BACH. Ueber die Abhängigkeit der geotropischen Praesentations- und Reaktionszeit von verschiedenen Aussenbedingungen. Jahrb. für wiss. Botanik. Bd. XLIV. 1907, p. 86.

(October 28, 1908).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETINGS
of Saturday October 31, 1908.

(Translated from: Verslag van de gewone vergaderingen der Wis- en Natuurkundige
Afdeling van Zaterdag 31 October 1908, Dl. XVII).

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Geology. — “*On the behaviour of fossil shells in water containing carbonic acid.*” By Dr. P. TESCH. (Communicated by Prof. S. HOOGWERFF).

(Communicated in the meeting of September 26, 1908).

It is a well-known phenomenon that all strata which are more or less calcareous and are situated above the surface of the ground-water, when not consisting of wholly impenetrable clay, are exposed to a slow action of solution. The explanation of this extraction of lime is easily given by the dissolving action of the penetrating rain-water, by which the quantity of lime is gradually withdrawn from the higher parts of the deposit and in some cases is concentrated in the lower parts in marl-puppets (for instance in the löss), in other cases, however is totally carried off (as a boulder-marl can be transformed in a clay without any lime). The rain-water contains already a good deal of oxygen and carbonic acid; the part that sinks away in the bottom still takes up the carbonic acid which is formed in the upper-crust by the putrefaction of the vegetable rests and thus it is enabled to exercise an oxidating action on the iron-containing minerals and a dissolving action on the present lime.

Especially the fossiliferous glauconitic sands are totally changed by this alteration. In the first place the glauconite is dissected and the iron which for a great part exists already in the ferri-form, is separated as limonite and forms a binding for the grains of sand. The sand in the beginning of a dark or light green changes into a yellow or brown sand, which in some cases is bound so strongly that the name of a limonite sandstone may be given. Everywhere where glauconitic sands are situated above the surface of the ground-water and are not covered by protecting clay-beds, this phenomenon can be observed. In the southern parts of the Lower Rhine basin for instance the upper-oligocene sea-sands show everywhere where they have kept their original niveau, a yellow or brown colour by the disintegration and oxidation of the glauconite grains (heaved block of Myhl between Hückelhoven and Birgelen on the eastern bank of the Roer, the sandquarries of Gerresheim, Grafenberg and Rothenberg east of Dusseldorf etc.). In Belgium the “sables et grès ferrugineux de Diest”, the “Crag jaune d’Anvers” etc. are so converted glauconitic sands.

In the second place however the water with carbonic acid acts as a solvent upon the lime shells of the fossils, which disappear totally or rest as printings and stones and are more difficult to

determine, in consequence of which the direct remedy of fixing the age fails or at least becomes uncertain. Especially in Belgium the division of the upper-tertiary deposits has given rise to many contradictions during a long time because the incomplete and indistinct fauna opposed the question of the exact parallelism with similar strata in a high degree. Only by the extensive researches of E. VAN DEN BROECK and others in the Antwerpian pliocene, when those deposits were uncovered on a large scale by the establishment of harbours and docks, this alteration was recognized as a general secondary action which appears everywhere where the circumstances of penetrable cover and a situation above the level of the ground-water allow it. The limit between the decomposed glauconite sand (yellow crag) and the original sand (gray crag) is not at all to be considered as a geological limit but denotes only the level of the ground-water.

I have mentioned these well-known facts in order to arrive at another observation which was made by inquiring the altered deposits and for which an acceptable explanation was ready. It was fixed that the resistance of the different shells against the dissolving action was a different one and thus more and less resisting shells were to be distinguished. The still recognizable stones and printings belonging to the genera *Terebratula*, *Ostrea*, *Pecten*, etc. and these shells being known to consist of calcite, while the small gastropoda shells are composed of aragonite, it was concluded that *calcite is dissolved in water containing carbonic acid with much more difficulty than aragonite*. In the "Handbuch der Palaeontologie" of KARL A. VON ZITTEL (Volume II, page 12) for instance this is expressed as follows:

"Die Kalkspathschalen zeigen eine ziemlich beträchtliche, die Aragonitschalen eine sehr geringe Widerstandsfähigkeit gegen die auflösende Thätigkeit kohlen säurehaltiger Gewässer. In Ablagerungen, wo fast alle fossilen Muscheln oder Schneckengehäuse zerstört und nur durch Steinkerne angedeutet sind, findet man wohlerhaltene Schalen von OSTREA, PECTEN, PINNA, TRICHTES, u. a."

I do not know whether this fact ever has been examined by experiments upon the pure minerals. The failing of any communication concerning that subject in different mineralogical test-books suggests that this has not taken place and thus it may be useful to examine this different behaviour experimentally, so far as the difference of solubility has an importance for the practical geology ¹⁾.

¹⁾ Some time after having finished this communication I got acquainted with an essay of H. W. FOOTE: Ueber die physikalisch-chemischen Beziehungen zwischen Aragonit und Calcit (Zeitschrift für physikalische Chemie, Band 33, pag. 740) to

A. Solubility of calcite and aragonite in pure water.

In all following experiments were used: for calcite fragments of the calcite of Iceland and for aragonite crystals of BILIN in Bohemia.

By pulverizing and sieving a powder was obtained the grains of which were all smaller than 2 mm. and larger than 1 mm. in order to equalize the circumstances.

To compare the solubility of the two minerals in pure water, a quantity of 1 or 2 grams of this powder was exposed during a week to 200 cm³. of newly distilled water and afterwards the quantity was again weighed accurately.

I obtained the result that the same quantity of pure water in the same time dissolved:

from the calcite powder:

4,8 milligrams

5,0 „

5,1 „

and from the aragonite powder:

2,8 milligrams

3,0 „

3,2 „

On these numbers a remark is to be made, to which prof. Dr. G. A. F. MOLENGRAEFF drew my attention. The grains of calcite will have the form of the cleavage rhomboeder and will moreover show small internal fissures. This has the consequence that the attackable surface offered by the calcite powder is much larger than that of the aragonite powder.

For this reason I experimented another time with the finest powder of the two minerals which had passed a silk sieve of 64 openings on the m.M.². I acted during the same time with the same quantities.

which Prof. Dr. S. HOOGWERFF drew my attention. According to the law that of two forms the least soluble is the most durable, the author finds in different ways that under the normal circumstances of pressure and temperature calcite is more durable than aragonite. Formerly it had already been shown by experiments of KOHLRAUSCH and ROSE that at the temperatures between 2° and 34° C. calcite is somewhat less dissoluble in water than aragonite. The author finds the same fact at the temperatures 25°, 50° and 59° C. By means of the electric properties the difference in solubility in water containing carbonic acid is examined at the temperatures of 8°, 25°, 41° and 48° C. At 49° C. aragonite is still 11% more soluble than calcite, though the difference becomes smaller at rising temperature.

The relations of solubility found in this essay agree satisfactorily with the results found by me by direct weighing.

taining carbonic acid than calcite. At the same time it is evident however that the difference of solubility is too small to serve for a practical remedy of determination.

2. that this little difference is not sufficient to explain the different behaviour of the fossil lime-shells, but that we must be taken into consideration still other causes: the long duration of the dissolving action, the continuous supply of new liquor, the absolute size of the shells and the relative size of the outer surface.

One finds in the common test-books the notice that 100 grams of water containing carbonic acid dissolve 0,1 or 0,12 grams of calcite which agrees sufficiently with the number mentioned above ¹⁾.

When examining the mineralogical composition of some shells, the question rose what remedy is the most suitable to distinguish calcite from aragonite practically. The little difference in hardness is of no use to this purpose, as a small quantity of silex may neutralize this difference. A calcite shell for instance may equal locally the hardness of aragonite by mixed silex and a determination depending only on this property seems precarious. Nor is the specific weight to be used as a certain quantity of silex, phosphatic lime, magnesia carbonate and organic materials influences it. On the contrary the test with dilute cobaltcarbonate solution of W. MEIGEN is very useful (Centralblatt für Mineralogie, Geologie und Palaeontologie, Jahrgang 1901, Seite 577). With the aid of this test I examined a number of shells of the following genera, availing myself in some dubious cases of the optical properties.

Of *calcite* consisted:

- Ostrea (recent, pliocene and senon,
- Pecten (recent, pliocene and senon)
- Pectunculus (miocene)
- Arca (miocene)
- Nucula (miocene)
- Leda (miocene)
- Venus (miocene)
- Cytherea (miocene)
- Isocardia (miocene)
- Littorina (recent)
- Buccinum (recent)
- Aporrhais (miocene)
- Ancillaria (miocene)

¹⁾ Here it must still be added that all these experiments took place at the common chamber temperature (15° or 20° C.) and that the glasses were shaken once a day in order to promote the action of the dissolving liquor.

Of *aragonite* consisted :

Cardium (recent and pliocene)
 Ensis (recent and pliocene)
 Donax (recent and pliocene)
 Tellina (recent and pliocene)
 Astarte (pliocene)
 Cardita (pliocene)
 Cytherea* (recent)
 Venus (recent)
 Unio (recent)
 Mactra (recent and pliocene)
 Mya (recent)
 Corbula (recent and pliocene)
 Pholas (recent)
 Scalaria (recent)
 Natica (recent)
 Cypraea (recent)
 Turritella (miocene)
 Cancellaria (miocene)
 Cassidaria (miocene)
 Cerithium (recent)
 Murex (recent)
 Conus (recent and miocene)
 Trochus (recent)
 Turbo (recent)
 Bulla (recent)
 Strombus (recent)
 Ficula (recent)
 Terebra (recent, miocene)
 Niso (miocene)
 Dentalium (pliocene, miocene and oligocene)
 Ringicula (miocene)

On looking through the above list it is evident that a great deal of the examined Lamellibranchiata consists of aragonite though among the fossil species enough calcite shells occur. A specimen of the miocene *Cytherea incrassata* consists without any doubt of calcite and a specimen of the recent *Cytherea meretrix* consists with the same certainty of aragonite. Such was also the case with the miocene *Venus multilamellosa* and the recent *Venus albina*. Among the Gastropoda shells the majority consists of aragonite but four shells form an exception. For the fossil specimina of *Aporrhais* and *Ancil-*

laría perhaps it is permitted to think of a later inversion of aragonite into calcite but for the very new specimens of *Buccinum undatum* and *Littorina littorea* this explanation seems excluded. Possibly the form in which the lime carbonate is separated depends on external influences and a species which builds as a rule an aragonite shell may be able to separate calcite under abnormal circumstances (temperature, composition of the water). This appears to me the more probable as we can precipitate artificially calcite or aragonite according to the circumstances of temperature and composition of the solution. If this should be true the composition of the shell is no specific property.

Geophysica. — “*Earthcurrent-Registration at Batavia.*” (3^d communication). By Dr. W. VAN BEMMELEN.

In the preceding communication about my earthcurrent registration in Java, I expected to be able before long to throw more light on the question of the abnormal intensity of the current between Batavia and Anjer (a place in the neighbouring residency of Bantam)

The kind co-operation of the Superintendent of Government Railways, who allowed me the use of the railway telegraph lines during night time, enabled me to realise my intention of measuring the currents flowing between Batavia and some other places situated in the residencies of Batavia and Bantam.

In order to obtain an exact control over the new results, I registered next to the currents flowing through these wires, those between Anjer and Batavia flowing through the direct telegraph line between these towns, i.e. by means of the line formerly used by me. Moreover the N—S component of the magnetic force was recorded.

By means of the railway telegraph-wires I obtained connection with the following places:

Laboean on the Westcoast of Java, 32 K.M. to the S.S.W. of Anjer.
Serang 28 K.M. to the East of Anjer.

Rangkas Betoeang 40 K.M. to the East of Laboean.

Between Anjer, Serang, Rangkas Betoeang and Laboean there rises a volcanic chain, the volcano Karang (1780 M.) being the culminating summit.

Tangerang 21 K.M. to the West of Batavia.

Bekassi 20 „ „ „ E.S.E. „ „

Krawang 54 „ „ „ E.S.E. „ „

The directions and distances from Batavia are :

Batavia—Anjer	W 5°N.
„ Laboean	W 12 S.
„ Serang	W 4 N.
„ Rangkas Betoeng	W 17 S.
„ Tangerang	W 1 S.
„ Bekassi	E 17 S.
„ Krawang	E 14 S.

I think it necessary for a better understanding of the results to be mentioned hereafter, to summarise the results obtained before.

In my former work on earthcurrents I always compared the oscillations shown in the intensity of the current, with those occurring simultaneously in the magnetic component, always taking into account the horizontal component directed perpendicularly on the straight line connecting the two stations.

I measured the variations of the magnetic component in absolute measure, and determined those of the earthcurrent by means of the differences of potential per Kilometer, which, if existing, should give the same variation of the current through the wire as was shown by the recording galvanometer.

Thus I did not decide whether such a difference of potential really existed at the two stations.

The records obtained brought to view the fact, that especially for places one of which lies to the East of the other, each oscillation of the earthcurrent corresponded with a simultaneous one of the component. But if one station lies to the North of the other the correspondence with the E.-W. component of magnetic force was much less than in the former case.

The connection between corresponding oscillations of earthcurrent and magnetic force may be described thus. Those of the earthcurrent precede those of force with a certain difference of phase; their amplitude increases compared with those of force, when the duration decreases.

As to the amount of this difference of phase and of this increase of amplitude I found them to be quite different for the coast-plains of North-Java and the volcanic regions in the southern part of the island.

In the South especially the increase of amplitude, which accompanies decreasing duration, was much more rapid, than in the northern regions. The following figures will make this divergence evident.

Mean half duration of the oscillation	Amplitude of earthcurrent in volts. per K.M. Amplitude of magnetic force	
	Northern-Java Batavia-Cheribon	Southern-Java Buitenzorg-Tasik Melaja
0.5 min.	21.2	59.0
1.2 "	20.5	55.0
90 "	16.5	15.0

I recorded the current between Semarang and Cheribon and between Semarang and Soerabaja during a stay at the former place and found it to be of the same type and strength as the current between Batavia and Cheribon. The current between Batavia and Anjer however, though bearing also this same type, I found to be more than four times stronger. Experiments made specially for that purpose giving evidence of the reality of this phenomenon, the next step to be done was to examine the current between Batavia and other places situated between Anjer and Cheribon. In the months of March and April of this year I made these measurements, having recorded during some nights the current for each station in connection with Batavia, together with the Batavia—Anjer current and the N—S component of magnetic force.

I measured on the diagram obtained the amplitudes for a certain number of oscillations of short and of longer duration; the average values are given below. For each case I have added the proportion of the strength of the currents (per K.M.) to that of the Anjer-current. (See table p. 245).

When we examine the numbers of the last column, which give the proportion of the strength of the currents between Batavia and Anjer we at once see that for each case this proportion is nearly the same for shorter and longer oscillations (only for Batavia-Bekassi we find an exception, the numbers being 1.9 and 1.3 resp.).

Now this means that also for different regions between Anjer and Cheribon the currents bear the type of the coast-plains of northern Java, as was mentioned above.

But the numbers also point to a gradual increase of strength, when we connect successively Batavia with places of an increasing westerly position.

Supposing the current between Batavia and Cheribon to be 1.0,

Earth-magnetical E-W component		Earth-current			
Half duration of the oscillation	Amplitude	Amplitude of the Earthcurrent in V.p. KM. Ampl. of the magn. force in abs. meas.			Ampl. Btv.-Anjer Ampl. Btv.-Station
		1.3 min.	1.27	Batavia—Laboean	
7.3	2.8	” ”	60	” ” 62	1.1
0.5	1.6	Batavia—Serang	86	” ” 97	1.1
2.0	0.9	” ”	66	” ” 75	1.1
9.6	3.3	” ”	57	” ” 68	1.2
0.9	0.5	Batavia—Rangkas Betoeng	80	” ” 82	1.0
10.0	1.2	” ” ”	52	” ” 47	0.9
0.5	1.0	Batavia—Tangerang	49	” ” 97	2.1
6 2	0 8	” ”	39	” ” 82	2.0
0.5	0 9	Batavia—Bekassi	47	” ” 89	1.9
13.7	7.5	” ”	43	” ” 57	1.3
0.7	0.4	Batavia—Krawang	25	” ” 93	3.7
13.7	2.8	” ”	20	” ” 72	3.6
		Batavia—Cheribon			4.2

we have, taken into account the variations of the current during short oscillations only :

	Amplitude Earthcurrent
Batavia—Cheribon	1.0
” Krawang	1.1
” Bekassi	2.2
” Tangerang	2.0
” Rangkas Betoeng	4.2
” Serang	3.8
” Anjer	4.2
” Laboean	3.5

If we suppose, that a difference of potential rises between Cheribon and Batavia, when a certain variation of the magnetic force occurs, and supposing the gradient of potential to be 1 Volt per K.M., we are able to calculate the potentials rising at the different stations.

For convenience, sake we may assume the potential at Cheribon to be zero. We find :

Laboean	595	volt
Anjer	645	„
Serang	496	„
Rangkas Betoeng	481	„
Tangerang	242	„
Batavia	200	„
Bekassi	156	„
Krawang	141	„
Cheribon	0	„

From these and formerly found values we deduce the following gradients.

Between	Potent. gradient	Geological formation.
Anjer and Serang	5.3	Neo-volcanic
Serang and Tangerang.	4.5	Quaternary
Rangkas Betoeng and Tangerang	4.4	Quaternary
Tangerang and Bekassi	2.1	Quaternary and alluvium
Bekassi and Krawang	0.4	Alluvium
Krawang and Cheribon	1.0	Quaternary and alluvium
Cheribon and Semarang	0.9	Quaternary and cretaceous
Semarang and Soerabaja	1.1	Quaternary, cretaceous a. alluvium.

The geological formations encountered on the different passages, have been borrowed from the geological atlas of VERBEEK and FENNEMA.

It is not to be denied, that a certain connection seems to exist between gradient and formation, such that the gradient is least in alluvium, greater in quaternary and greatest in the volcanic layers; and neither may it be said, that this succession is improbable.

Also for the volcanic province of the Preanger in southern Java I found a high value, viz. 3, but here the proportion of amplitudes for current and force bears the other type, which involves the gradient to be small, viz. 1, for oscillations of longer duration.

The formations given by the geological atlas are those met with at the surface of the earth, and the outlines of the deeper layers, no doubt, will differ much from those of the superficial ones.

Thus when we find a connection between the strength of the current and the outlines of the superficial layers, this points out that the currents measured are the superficial ones too.

Accordingly it is no wonder that the currents bear a different type in the mountainous Preanger compared with those of the coast-plains; but I utterly fail to explain this difference, just as it has been found.

All that has become known till now points to the next step, which should be taken in this research, viz. that the earth-connections should be brought to a depth of, say one or more kilometers under the surface of the earth, but, alas this is impossible.

It is true I had the intention to make use of two artesian wells to be bored recently at Serang and Batavia, but the considerations, that first the mantle of these holes consisted of iron, the depth was only 0,2 à 0,3 K.M., and besides the wire connecting the two did not possess the necessary isolation, frightened me out of this burdensome experiment.

I think it advisable to continue the registration in the old way, but to take into account the geological formation in the first place.

Dr. L. STEINER of Budapest has directed my attention to the fact, that I have erroneously applied the formula $A = 0.8 \sqrt[4]{\frac{1}{TM}}$ (c.f. 1st Comm. Proc. Jan. 25, 1908. p. 515) on the harmonic terms of the daily variation for the earthcurrent between Batavia and Cheribon.

Indeed a calculating error has curiously given rise to an apparent agreement between the observed values and those computed by means of the formula.

Dr. STEINER deduced the following expression

$$\frac{A}{M} = 3.9 \frac{1}{T^{0.8}} \text{ or } \frac{A}{M} = 3.9 \frac{T^{0.2}}{T}$$

This formula gives the following values

Amplitude					
	Earth-current volt. p. KM. $\times 10^{-5}$	Magn. Comp. c. g. s. $\times 10^{-5}$	Earth-current Magn. comp.		Δ C—O
			Observ.	Calc.	
A_1	74.6	18.62	4.0	3.9	— 0.1
A_2	43.8	7.63	5.7	6.6	0.9
A_3	27.7	2.96	9.4	8.9	— 0.5
A_4	8.9	0.90	9.9	10.8	0.9
A_5	6.9	0.53	13.0	13.0	0.0
A_6	6.6	0.42	15.7	15.0	— 0.7

He also remarks that this formula agrees in character with my theoretical one, viz.

$$\frac{A}{M} = C \frac{\rho}{1 + c'} \cdot \frac{1}{T}$$

because $1 + c'$ slowly increases with decreasing T .

This, indeed is the case. For instance when we assume $\rho = 3.70 \times 10^{13}$ or $\sigma = 10$, and consider the spherical function of order 2 we find after SCHUSTER (Phil. Tr. Vol. 180 p. 496):

σ	$1 + c'$	$\frac{1 + c'}{1.172}$
1	1.019	$0.869 = 0.1^{0.061}$
5	1.093	$0.933 = 0.5^{0.100}$
10	1.172	1.000 —
20	1.278	$1.091 = 2^{0.126}$
30	1.337	$1.141 = 3^{0.120}$
40	1.374	$1.173 = 4^{0.115}$
50	1.399	$1.194 = 5^{0.110}$
100	1.466	$1.251 = 10^{0.097}$

The exponent accordingly changes slowly, and reaches as a maximum 0.126, a value, which approaches the value 0.2 required by the empirical formula.

I think this points to a possibility to bring agreement between the theoretical assumptions and the observed facts for the daily variation of earth-current and magnetic component. However this is not the case for the short oscillations.

I regret that my near return to Europe prevents me from entering now on those questions, or making new experiments.

Batavia, Aug. 1908.

Chemistry. — “*The nitration of toluene*”, by Prof. A. F. HOLLEMAN.

(Communicated in the meeting, of September 26 1908).

On account of its great technical importance the nitration of toluene has been studied repeatedly; the determination of the quantity of *o*- and *p*-nitrotoluene contained in the product of the reaction has also been carried out a few times. RAOUL PICTET, (C.R. **116**, 815) states that when toluene is nitrated at -55° 5.5 times as much *p*-nitrotoluene is formed as when the nitration is carried out at 0° . HOLDERMANN, (B. **39**, 1250) tried to modify the proportions in which

o- and *p*-nitrotoluene are formed by adding catalyzers (generally consisting of metallic salts) to the mixture of nitric and sulphuric acid used in the nitration. The amount of *o*-nitrotoluene present in the product of nitration only varied however from 57.16 to 60.85%. In these experiments the temperature was kept between 5 and 10°. When nitrated at 0° with nitric acid (sp. gr. 1.52) 52.7% of nitro-toluene was obtained; on addition of different salts (the proportions are not stated) to this acid the quantity of *o*-compound diminished and when nickel sulphate was added it even got as low as 45.5%.

FRISWELL, (C. Bl. 1908¹, 2092) nitrated toluene under many various conditions in order to increase the yield of *p*-nitrotoluene. He obtained however, always 60—65% of *ortho*- and 40—35% of *para*-compound.

None of these chemists make any statement as to the method used in these determinations, although HOLDERMANN expresses his results even in two decimals. As will be noticed from the above quotations the figures differ widely. Moreover, NÖLTING (B. **12**, 443; **18**, 1337) has shown that the nitration product of toluene contains *m*-nitrotoluene the amount of which he estimates at 1—2%. It is, therefore, obvious that there is, as yet, no question of a fairly accurate knowledge as to the composition of the product of nitration of toluene, and, for this reason, I instructed Mr. VAN DEN AREND to determine the composition, with the aid of the more accurate methods, which for that purpose have been worked out in my laboratory. In this particular case the method of the solidifying points was the most practical one.

In order to apply the same, it is necessary to procure, first of all, the three *mononitrotoluenes* in an absolutely pure condition. A preparation of *o*-nitrotoluene of great purity has been obtainable for the last few years from MEISTER, LUCIUS and BRÜNING. A specimen received previously from that firm still contained 0.4% of *p*-nitrotoluene (These Proc. VII, p. 395). At my request they were kind enough to once more purify a sample of this almost pure *o*-nitrotoluene by freezing, and to place two kilos of the purified preparation at my disposal, for which I express to that firm my sincere thanks. This was found to contain only 0.13% of *p*-nitrotoluene and was used by Mr. VAN DEN AREND in his experiments without any further purification, except a single distillation in order to remove the dissolved water; a correction was then applied for the *p*-compound content.

It was shown that the methods proposed by REVERDIN and LA HARPE (Beilsteins Handbuch II, 91) and by LOESNER, (J. pr Chem. (2) **50**, 567) to free *o*-nitrotoluene from any *p*-nitrotoluene present are quite useless. *o*-Nitrotoluene is dimorphous; the melting points of the two modifications were determined by VAN DEN AREND by means of his

preparation and found to be $-3^{\circ}.7$ and $-9^{\circ}.4$. According to his observation the unstable modification with the higher m.p. is formed most readily when the liquid substance is cooled rapidly to about -30° . First, a solid yellowish mass is formed, which, on further lowering of the temperature, begins to show white spots and then turns quite white, with production of a crushing sound; the crystalline mass thus obtained melts at about -4° .

m-Nitrotoluene is obtainable from DE HAEN in a very pure condition. It was fractionated a few times when the melting point was found to be $+16^{\circ}$ and the boiling point $230-231^{\circ}$ at 756 mm.; it may therefore, be taken as pure.

p-Nitrotoluene from KAHLBAUM was recrystallised twice from alcohol and then distilled in vacuo; its solidifying point was found to be $54^{\circ}.4$.

Solidifying curve of o- and p-nitrotoluene.

<i>% para</i> -nitrotoluene	initial solidifying point	end solidifying point
100.0	+ $54^{\circ}.4$	—
97.5	$50^{\circ}.0$	—
91.6	$46^{\circ}.2$	—
79.0	$38^{\circ}.5$	—
72.9	$33^{\circ}.8$	—
67.5	$30^{\circ}.4$	—
60.5	$24^{\circ}.4$	—
46.6	$11^{\circ}.6$	— $15^{\circ}.0$
42.3	$5^{\circ}.4$	$15^{\circ}.2$
39.8	$1^{\circ}.8$	$15^{\circ}.7$
<i>% para</i> -nitrotoluene	initial solidifying point	end solidifying point
37.2	— $1^{\circ}.2$	$14^{\circ}.6$
33.5	$6^{\circ}.8$	—
30.6	$14^{\circ}.8$	—
24.9	$14^{\circ}.4$	$15^{\circ}.6$
16.3	$12^{\circ}.1$	—
11.2	$11^{\circ}.3$	—
0.0	$0^{\circ}.4$	—
		mean — $15^{\circ}.2$

Fig. 1 represents the solidifying curve constructed with the aid of these figures.

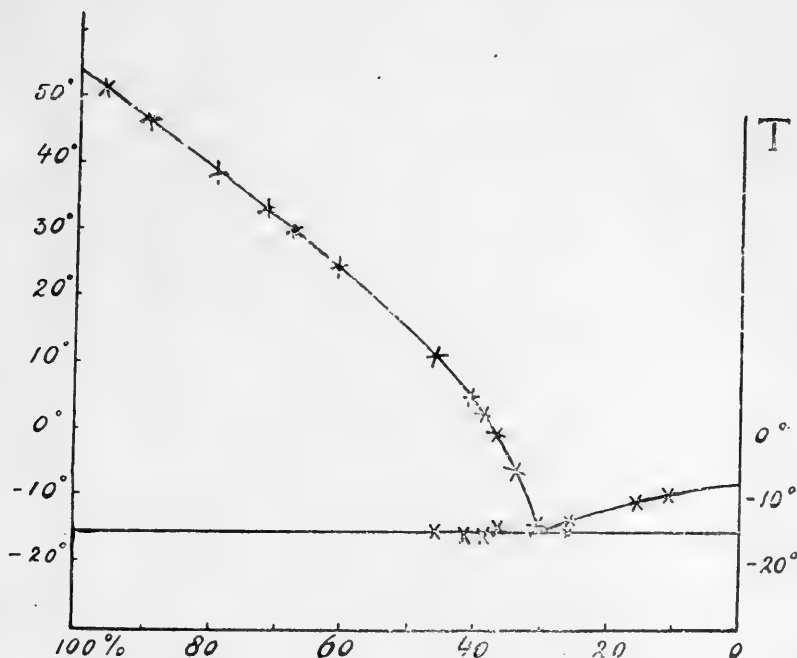


Fig. 1. Melting point curve of *o*- and *p*-nitrotoluene.

MR. VAN DEN AREND found the following figures for the specific gravities of *o*- and *p*-nitrotoluene and for some of their mixtures, at 80°.0:

100	%	<i>p</i> -nitrotoluene . . .	1.0981	calculated from
89.4	„	„	1.0993	the sp. gr. of <i>o</i> - and
68.4	„	„	1.1007	of <i>p</i> -nitrotoluene
61.0	„	„	1.1014	1.1006
46.5	„	„	1.1023	1.1015
32.0	„	„	1.1033	
0.0	(100	% <i>o</i> -nitrotoluene . .	1.1045 ¹⁾	

The figures calculated are those which may be deduced from the specific gravities of the isomers without contraction taking place. The graphic representation of these figures gives the subjoined diagram

1) Dr S. VAN DORSSEX has also at my request determined the specific gravities of *o*- and *p*-nitrotoluene by means of an EYKMAN'S pycnometer verified by himself and found as the average result at 80°.0 of four and three determinations respectively: *o*-nitrotoluene 1.1050; *p* nitrotoluene 1.0993, values which are both a little greater than those of VAN DEN AREND. All the values have been corrected for vacuum and the expansion of the glass. I will, however, use v. D. AREND'S figures because he has made all his determinations with the same pycnometer and therefore the results are sure to be mutually comparable.

which plainly shows the contraction which takes place on mixing the isomers, by the higher sp. gr. which the mixtures possess, in comparison with the calculated values (the straight line).

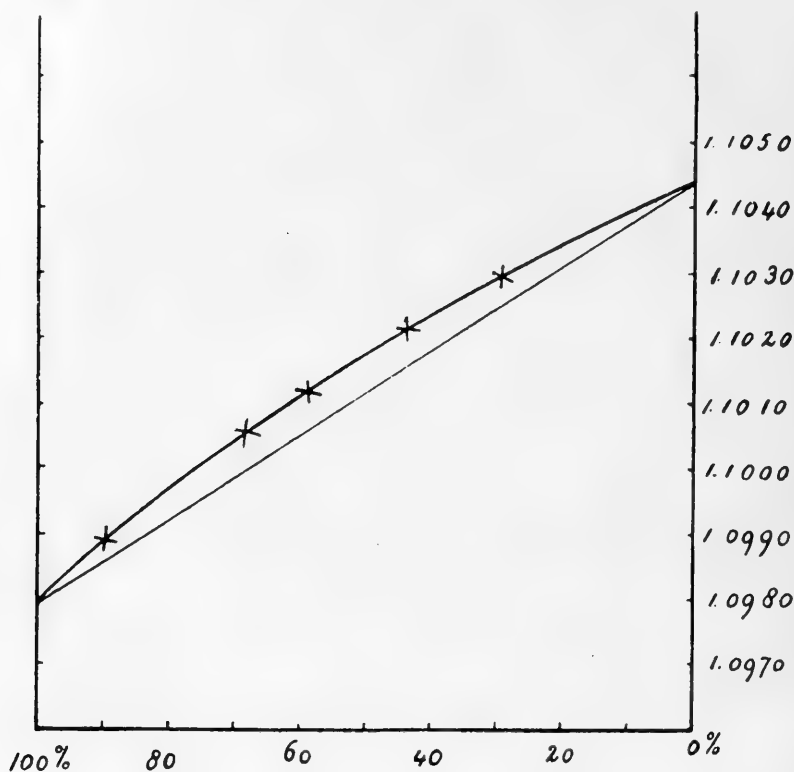


Fig. 2. Line of the specific gravities of *ortho*- and *para*-nitrotoluene.

The nitration of toluene was carried out by the method of BEILSTEIN and KUHMBERG, (A. **158**, 348), i.e. the nitric acid being added to the toluene and not reversedly, because, by their method, the formation of dinitro-products is entirely avoided. The toluene employed had a constant boiling point (110°.8 at 760 mm.) and had been purified by being boiled with sodium wire in a reflex apparatus.

The nitration of the purified toluene took place at the temperature of -30° ; 0° ; $+30^{\circ}$ and $+60^{\circ}$ and was carried out as follows:

75 grams of the toluene were placed in a small flask and brought to the required temperature. 200 c.c. of nitric acid (sp.gr. 1.475) were slowly dropped into the toluene, the mixture being stirred mechanically. Immediately after the addition of the first drops of the acid the liquid turned intensely brownish-red; so that it was not possible to see whether two liquid layers or one homogeneous mixture was formed. The heat evolved during the nitration was but trifling, at

least at 0°. After some time, the mixture was shaken repeatedly in a large separation funnel with water until no more acid reaction could be observed.

Being dried over sodium sulphate, the product was distilled in vacuo. The temperature was first kept for some time at 40°, to remove any unattacked toluene; at a pressure of 1 to 2 m.m. and a temperature of 90°—100° the whole distilled over leaving but a very small residue. Towards the end of the distillation much of the *p*-nitrotoluene passed over, which deposited in the exit tube as a yellow crystalline mass.

The distillate consisted of a clear pale yellow liquid.

After the solidifying point and the sp.gr. of such a nitration-mixture had been determined the distillation in vacuo was once more repeated and the solidifying point and the sp. gr. determined again. These did not differ perceptibly from the first ones.

The end solidifying points could also be determined pretty sharply; the subjoined table shows the results obtained:

Nitration at :			Spec. Gr.
— 30°	initial solidifying point	+ 4°.1	1.1026
	end " "	— 16°.6	
0°	initial " "	+ 2°.8	1.1026
	end " "	— 16°.8	
+ 30°	initial " "	+ 1°.4	1.1027
	end " "	— 16°.9	
+ 60°	initial " "	— 0°.8	1.1028
	end " "	— 17°.4	

The specific gravities were again determined at the temperature of boiling benzene and reduced to 80°.0. They have been corrected for vacuum and expansion of the glass.

I have had these observations repeated in part by Messrs CALAND, VAN DORSSEN and DE LEEUW who have themselves purified toluene in the manner described, nitrated the same, and determined the initial and end solidifying point, also the sp. gr. of their nitration product. They found:

Nitration at :			Sp. Gr.
0°	initial solidifying point :	+ 1°.0 ; + 2°.7	1.1026
	end " " :	— 18°.1 ; — 18°.4 ; — 18°.2	
60°	initial " " :	+ 3°.1	1.1023
	end " " :	— 18°.5	

The end solidifying points were found to be a little lower; as regards the initial solidifying point of $+3^{\circ}.1$ in the nitration at 60° it should be observed that the mixture of toluene and nitric acid had been left over night and separated into two layers which was not the case in VAN DEN AREND'S experiment. With an initial solidifying point of $-0^{\circ}.8$ corresponds 37.5% of *p*-nitrotoluene; with that of $+3^{\circ}.1$, 40.7%, disregarding, for the moment, the small quantity of *m*-nitrotoluene present in the nitration product. As a content of 40.7% of *p*-nitrotoluene corresponds with a sp. gr. of 1.1026 it seems that no higher nitration products are formed, even at $+60^{\circ}$, when the nitration is carried out in the manner indicated. This is also shown by the position of the end solidifying point which is but little lower than that found with the nitration products obtained at lower temperatures.

In order to determine the *o*-, *m*- and *p*-nitrotoluene content of the nitration product it must be regarded as a ternary mixture, and the lowering which the initial and end solidifying points undergo, on adding a small quantity of *m*-nitrotoluene, should be determined, as NÖLTING'S investigation had shown that the latter is present only to the extent of a few %.

A mixture of pure *o*- and *p*-nitrotoluene weighing 2.8319 grams, composed of 35.5% *para*- and 64.5% *ortho*-nitrotoluene, had an initial solidifying point $-3^{\circ}.8$ and an end solidifying point $-14^{\circ}.9$.

If now 0.0860 grams of 2.9% of *meta*nitrotoluene were added, the initial solidifying point fell to $-6^{\circ}.0$, the end solidifying point to $-16^{\circ}.7$.

The percentage of *o*- and *p*-nitrotoluene in the mixed nitration product at 0° , with an initial solidifying point $+2^{\circ}.8$ and an end solidifying point $-16^{\circ}.8$ could now be determined in the following manner, keeping account of the *meta*-compound formed.

On addition of 2.9% of *meta* the end solidifying point falls from $-14^{\circ}.9$ to $-16^{\circ}.7 = 1^{\circ}.8$. Owing to the presence of *meta*-nitrotoluene, the end solidifying point of the mixed nitration product has been found to be $-16^{\circ}.8$ instead of $-14^{\circ}.9$ (the eutectic point of the mixture *ortho* + *para*), therefore $1^{\circ}.9$ lower. From this it follows that in the mixture at 0° there is present $\frac{1.9 \times 2.9}{1.8} = 3.1\%$ of *meta*.

Owing to the presence of those 2.9% of *meta*-compound, the initial solidifying point of the artificial mixture has fallen from $-3^{\circ}.8$ to $-6^{\circ}.0$, therefore $2^{\circ}.2$. For 3.1% of *meta* the fall must amount to $2^{\circ}.4$. If for the mixed nitration product is found an initial

solidifying point of $+2^{\circ}.8$, this would have been $5^{\circ}.2$ if no *meta*-compound were present, from which it follows that 42.2% of *para*- and 57.8% of *ortho*-nitrotoluene must have formed.

Applying this manner of calculation to the other mixed nitration products we found them to possess the following composition :

Nitration at	initial solidifying point	+	$^{\circ}$	$\%$ <i>para</i>	$\%$ <i>ortho</i>	$\%$ <i>meta</i>
-30°		$+4^{\circ}.1$		41.7	55.6	2.7
	end		$-16^{\circ}.6$			
0°		$+2^{\circ}.8$		40.9	56.0	3.1
	end		$-16^{\circ}.8$			
$+30^{\circ}$		$+1^{\circ}.4$		39.9	56.9	3.2
	end		$-16^{\circ}.9$			
$+60^{\circ}$		$-0^{\circ}.8$		38.5	57.5	4.0
	end		$-17^{\circ}.4$			

If the end solidifying point of the nitration product prepared at 0° is taken as $18^{\circ}.1$, namely, the mean of the figures found afterwards, the *meta* content increases and amounts to 5.3% . There remains, therefore a doubt of about 1% in regard to the quantity of *meta* compound present in the nitration product, if on the one hand we accept the mean of VAN DEN AREND'S values as the true solidifying points, and on the other hand the average values of the other investigations. But also for another reason the quantity of the *m*-compound cannot be determined more accurately.

In the above calculation various surmises have been made. It is for instance, supposed that, at least over the first course, the line which connects the binary eutecticum of *ortho*- and *para*-nitrotoluene with the ternary eutecticum is a straight line. It has also been taken for granted that the fall of the initial solidifying point is proportional to the addition of small quantities of a third isomer. An exact determination would be possible only when the entire ternary melting figure were constructed; yet the method as applied here gives a satisfactory approximation as will be seen from a survey of Fig. 3.

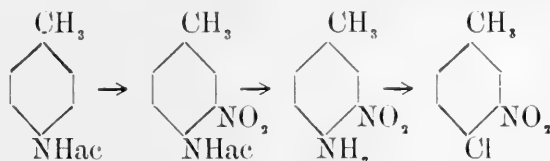
In the plane $OPO'P'$ is situated the melting point curve of *o*- and *p*-nitrotoluene. If, however, a small quantity of *m*-nitrotoluene is present we do not determine a point of the melting point curve $O'E'_1P'$, but a point of a curve situated on a line $O''E'_1P''$, which is obtained by carrying through the prism a plane parallel to the OP plane, and this at a distance from the OP plane corresponding with the amount of *meta* present. If an arbitrary mixture M consisting of *o*-, *p*- and *m*-nitrotoluene is cooled a separation of solid *ortho* or *para* will take place at a definite temperature; all depends on whether the mixture has the composition indicated by the right or the left melting

Chemistry. — “*The nitration of p-chlorotoluene.*” By Prof. A. F. HOLLEMAN.

The *p*-chlorotoluene required for this purpose was prepared by Mr. VAN DEN AREND from pure *p*-toluidine b. p. 160—161° at 754 mm.; m. p. + 7°. Of both nitro-*p*-chlorotoluenes the isomer



was obtained by him from *p*-chlorotoluene by nitration and separation of the mononitrocompounds; it melted at + 38°. He prepared the other isomer $\text{CH}_3, \text{Cl}, \text{NO}_2 = 1, 4, 3$ according to GATTERMANN'S method B. 18,1483 which may be expressed by the following scheme:



The product obtained had a boiling point of 259—260° at 759 mm. and melted at + 7° in a capillary tube. The solidifying point was + 5°8.

For the determination of the relative quantities of both isomers present in the nitration product of *p*-chlorotoluene the solidifying point determination process was again found to be the most suitable. Hence the solidifying point curve of these isomers had to be determined. Mr. VAN DEN AREND obtained the subjoined figures:

% 2-NO ₂ -4-Cl-toluene	Initial solidifying point	End solidifying point
100.0	+ 38°.2	—
57.0	+ 9°.7	—7°.9
44.7	+ 1°.4	—8°.2
34.8	— 6°.3	—
29.8	— 7°.2	—
24.1	— 4°.1	—8°.2
17.5	— 0°.5	—
14.1	+ 0°.4	—
6.6	+ 4°.5	—
0.0 (100% 3-NO ₂ -4-Cl-toluene)	+ 5°.8	—

Of these the following figure is the graphic representation.

For the sp. gravities of both isomers and for some of their mixtures, Mr. VAN DEN AREND found the following figures, corrected for upward air pressures and for the expansion of the glass of the pycnometer. The temperature was 80°.0.

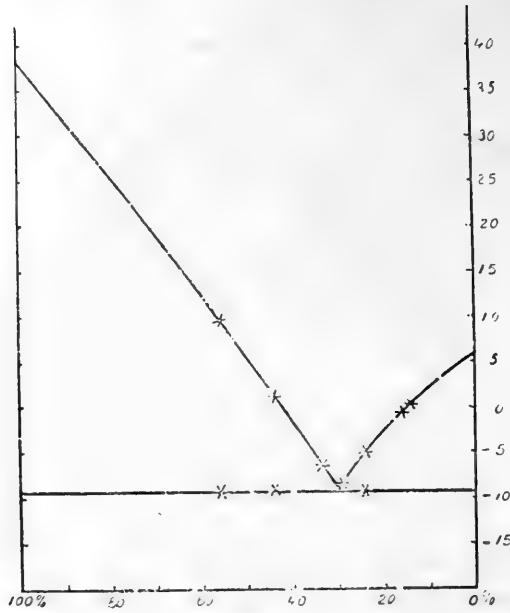


Fig. 1.

Solidifying point line of *p*- and *o*-nitrotoluene.

2-nitro-4-chlorotoluene	calculated
100%	1.2559
57.0	1.2477 1.2446
17.5	1.2364
0.0% (100% 3-nitro-4-chlorotoluene)	1.2296

In the subjoined graphic representation they have been united. The calculated value is the one which the sp. gr. ought to have according to the straight line in the figure, so without contraction. The latter is therefore rather considerable.

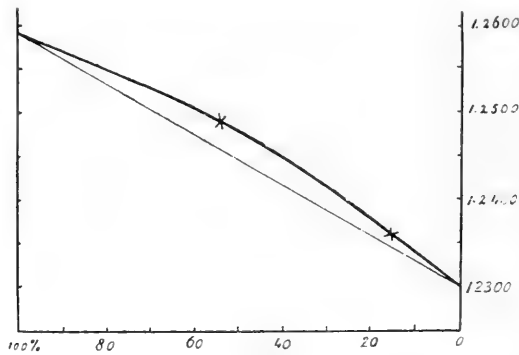


Fig. 2.

Line of the specific gravities for mixtures of the mono-nitro-para-chlorotoluenes.

It was only after some unsuccessful efforts that we succeeded in carrying out the nitration of *p*-chlorotoluene with nitric acid, in that sense that everything was just nitrated, without formation of any dinitro-products. Mr. VAN DEN AREND could ascertain this by determining the specific gravities. As in the case of pure toluene it was again found practical, in order to avoid the formation of higher products of nitration, to add the nitric acid to the *p*-chlorotoluene and not reversedly.

10 grams of *p*-chlorotoluene were cooled to 0°. At that temperature it solidifies to large leaf-like crystals; at the moment of crystallisation setting in, nitric acid (D. 1.48) was added, drop by drop, with thorough shaking. After 1 cc of acid had been added all the crystals had already fused. The liquid turns very dark and consists at first of two layers. After further addition of acid, the temperature being kept at 0° the colour turns pale yellow and the liquid becomes homogeneous. When this point was reached the further addition of acid was stopped and after a few moments the liquid was poured into water. In all, four times the weight of nitric acid was used. The pale yellow oil which collected at the bottom was agitated repeatedly with water until no further acid reaction was noticed, and then dried over sodium sulphate. The following day, the nitration product was distilled twice in vacuo when a slight black residue was left behind. The yield of purified product was 12 grams. It had an initial solidifying point of + 10°.2 and an end solidifying point of - 8°.0. From the first figure it follows that the nitration product must contain 58% of $\text{CH}_3\text{ClNO}_2 = 1, 4, 3$, whilst the figure for the end point, which coincides with the eutectic point, shows that the mixture contains no other substances besides these two. This was also proved by the sp. gr. which was found to be 1.2481 for an artificial mixture of this composition, whilst the nitration mixture possessed the same sp. gr. Mr. DE LEEUW who also nitrated *p*-chlorotoluene in the manner described, found the initial solidifying point of his product + 10°.9, the end point - 8°.3. This initial point corresponds with 58.8% 1.2.4.

Mr. VAN DEN AREND also mixed an artificial mixture of both isomers containing 58% 1.2.4 and 42% 1.3.4 with the nitration product in about equal quantities; the mixture so obtained solidified at + 10°.3.

It may, therefore, be taken as proved that the nitration product has the above composition. A chlorine determination according to Carius gave 20.3% (calculated 20.7%).

Two nitrations were carried out at + 30° in the manner described, using nitric acid (D. 1.45) which both yielded a product the sp. gr. of which was much too high. It appeared that at this

temperature higher substituted nitro-products were readily formed.

If the nitration is carried out at $+60^{\circ}$ a product is formed which solidifies at $-9^{\circ},2$, a temperature which is situated lower than the eutectic one of mixtures of the two pure components. The sp. gr. is 1.2626. No doubt considerable quantities of polyvalent nitro-compounds are formed at this high temperature of nitration.

Amsterdam, Org. chem. lab. Univ. Aug. '08.

Chemistry. — “*The quantitative estimation of the products of nitration of m-chloro and m-bromobenzoic acid.* By Prof. A. F. HOLLEMAN.

The above investigation has occupied me more than once.¹⁾ In the nitration of each of these acids two nitrohalogen acids are formed namely 1,6,3 = $\text{CO}_2\text{H}, \text{NO}_2, \text{Cl}(\text{Br})$ as main product and 1,2,3 = $\text{CO}_2\text{H}, \text{NO}_2, \text{Cl}(\text{Br})$ as byproduct; the question arose in what proportion these acids are present in the nitration mixture.

The reasons which induced me to revert to this investigation are twofold. Firstly, because the percentage of byproduct in the nitration mixture of *m*-chlorobenzoic acid was found 2.8% higher in the first investigation than in the second, when another method of analysis was applied and this difference was not satisfactorily explained. Secondly because it was found in the nitration of *o*-chloro- and *o*-bromobenzoic acid and also in that of *m*-chlorobenzoic acid, that more byproduct is formed at 0° than at -30° , whereas in the nitration of *m*-bromobenzoic acid the very opposite result was noticed.

In the first investigation the quantity of main product was determined by extracting the nitration mixture with benzene and determining the sp. gr. of the benzene solution. In the second determination the quantity of byproduct was deduced from the solidifying point of the mixture. A third *modus operandi* was followed for this renewed investigation, namely, the extraction of the nitration mixture with water and titration of the aqueous solution obtained.

I do not intend giving any further details of these methods as I described these repeatedly on former occasions.

MSSRS. J. J. POLAK and H. L. DE LEEUW, who have carried out these investigations independently, started from chemically pure preparations of *m*-chloro- and *m*-bromobenzoic acid, which were nitrated with absolute nitric acid after which the nitration product was collected according

¹⁾ R. 19 188, [1900] and R. 20, 223 [1908].

to the method given in *R.* 20, 223. I will only add that the complete removal of nitric acid from the product was effected with particular care as it appeared that this acid is retained with great obstinacy. In order to get the nitration product so pure that it gave, at the ordinary temperature, no, or but a feeble reaction with sulphuric acid and diphenylamine, it was necessary to wash it many times with cold water and to dry it over lime in vacuo. The organic acids, which had dissolved in the washings were, of course, recovered in the manner described previously. The removal of the last traces of nitric acid was of great importance in these determinations, because the presence of even very minute quantities of this acid causes, in the analytical method followed here, a too low percentage of the byproduct.

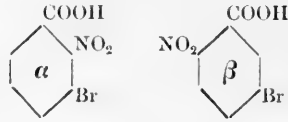
In this method about 0.4 gram of nitration mixture is extracted with 100 grams of water and the acidity estimated by titration with $\frac{n}{10}$ alkali. Suppose 1 mgr. of nitric acid ($= 0.25\%$) had been retained in that quantity it is sure to have dissolved together with the whole of the main product. 1 mgr. $= 0.016$ millimol. 1 cm.³ of the alkali corresponds with 0.1 millimol. so that 0.16 cm.³ or about 3 drops are required for neutralisation. As the molecular weight of chloronitrobenzoic acid is 201.5 and that of bromonitrobenzoic acid 246, 0.016 millimol. represents, respectively, a weight of 3.2 and 3.9 mgr. or of $\frac{3}{4}\%$ and 1% of the nitration mixture. The main product contained therein is therefore found too high and the byproduct correspondingly too low since the latter is found by difference. As the content in byproduct in these mixtures does not exceed 13% (in the bromo-acids) an error of 1% is a rather serious one.

In order to be able to determine the composition of the nitration mixtures by solubility determinations it was necessary to determine first for the chloro- and bromobenzoic acids, the solubility of the least soluble ones (in both cases the byproduct) and then the total solubility, when the liquid is kept saturated with this least soluble acid, but mixed with gradually increasing portions of the main product; when the liquid does not get saturated, all the main product passes into solution. By means of the solubility tables thus obtained the composition of an unknown mixture may be deduced reversedly by determining its solubility figure.

SOLUBILITY LINES.

Temperature 25.°0.

1. Bromonitrobenzoic acids



MW 246

Quantity of substance shaken with 100 cc. of water	Pipetted off	cc. of alkali (0.0287 <i>n</i>)	Total solubility in grams per 100 cc. of solution
100 mgrs. α	59.455 grs.	2.75	0.033
1 gram β	60.180 „	63.15	0.741
100mgrs. α + 118.8mgrs. β	26.211 „	5.00	0.135
„ + 203.7 „ „	32.345 „	9.90	0.216
„ + 299.0 „ „	31.050 „	13.60	0.309
„ + 402.0 „ „	19.021 „	11.00	0.408
„ + 497.6 „ „	20.173 „	15.65	0.502
„ + 587.3 „ „	20.337 „	17.05	0.592

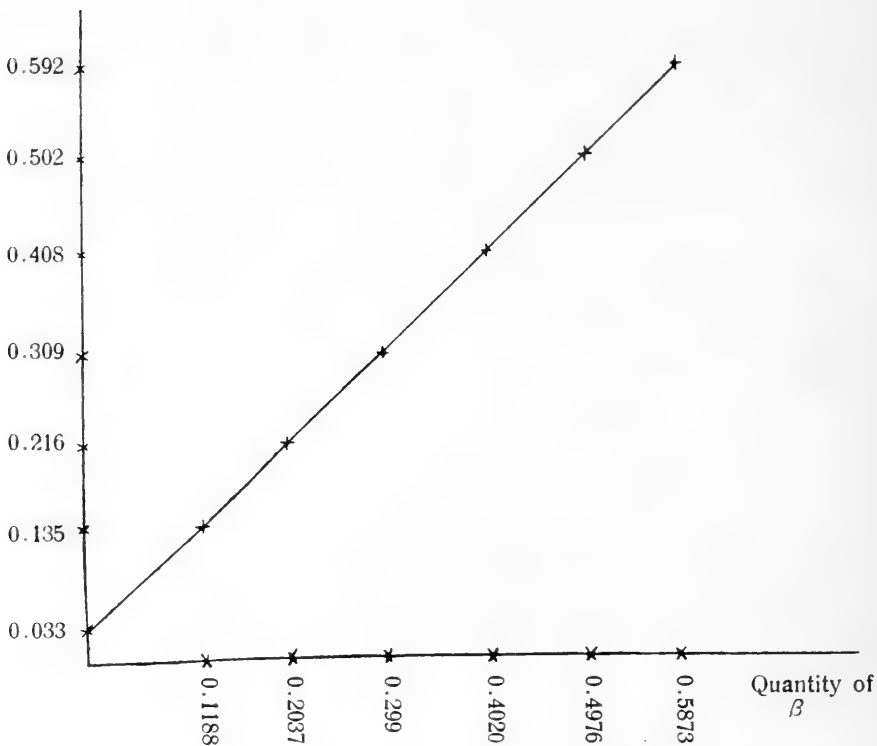
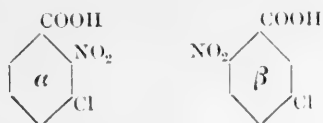


Fig. 1. Total solubility of mixtures of the bromonitrobenzoic acids constructed according to the table.

Duplicate determinations made by again titrating an aliquot portion from the bottles gave results within the limit of experimental error.

The graphic representation Fig. 1 shows that the line, except for a small deviation at the start, is a straight one.

2. *Chloronitrobenzoic acids.*



Temp. 25.°0 MW 201.5.

Quantity of substance shaken with 100 cc. of water	Pipetted off	cc. of alkali (0.0295 <i>n</i>)	Total solubility in grams per 100 cc. of solution
150 mgrs. α	37.611 grs.	3.0 cc.	0.047
1 gr. β	18.378 „	29.20	0.967
100 mgrs. $\alpha + 0.3020 \beta$	29.650 „	15.70	0.315
100 mgrs. $\alpha + 0.4120 \beta$	23.240 „	16.35	0.418

These titrations are accurate within 2 drops of 0.03 normal alkali. As this corresponds with about 0.7 mgr. of chloro- and 0.8 mgr. of bromonitrobenzoic acid the last figure of the numbers of the last column may be about one unit wrong. The tables have been constructed by Mr. POLAK.

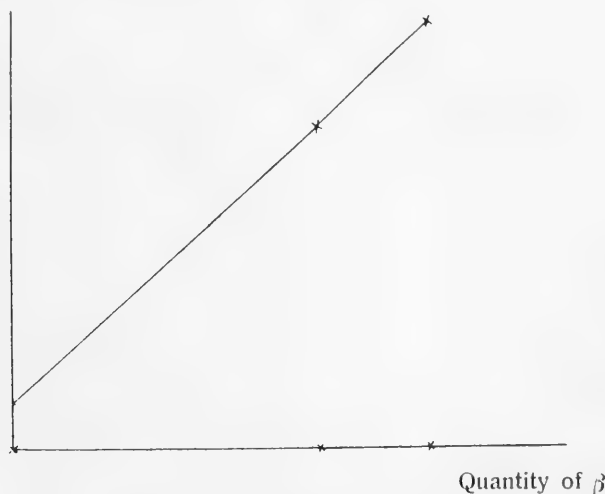


Fig. 2. Total solubility of mixtures of the chloronitrobenzoic acids, constructed according to the table.

As may be seen from fig. 2, the line is practically a straight one.

The nitrations of *m*-chloro- and *m*-bromobenzoic acid were carried out in the approved manner by means of absolute nitric acid at 0° and at -30°. In order to ascertain whether all had been converted into mononitro-acids the molecular weight of the products formed

was determined by titration. For this purpose 0.1 gram of the nitration mixture was dissolved in water and titrated with N/10 alkali; when using phenolphthaleine as indicator this titration is accurate within one drop. 0.1 gram is about 0.5 millimol of chloro- and 0.4 millimol of bromonitrobenzoic acid which require 5 and 4 cc. of N/10 alkali respectively. One drop (0.05 cc.) corresponds therefore, with 1% of the molecular weight of the chloro- or 0.8% of the bromo-acid. If now the molecular weight lies between 201.5 ± 2 or 246 ± 2 , respectively the substance may be taken to be pure nitro-acid. True it might be possible that, accidentally, a mixture had formed consisting of unattacked acid, mononitro- and dinitro-acid, which apparently possesses the molecular weight of the pure mononitro-acid but apart from the improbability that this should have formed, the possibility was also excluded, because the nitration mixture of *m*-bromobenzoic acid was again treated with absolute nitric-acid, which caused no serious alteration in the molecular weight. Mol. weight first 245; on repeated treatment 247.

Mr. DE LEEUW obtained the following results in the analysis of the nitration products prepared by himself.

I. Nitration of *m*-chlorobenzoic acid at 0°; 5 grams treated with 30 grams of absolute nitric acid.

Mol. weight of the product 203.2.

1. Weighed 381.9 mgrs. of nitration product; shaken with about 100 mgrs. of byproduct ($CO_2, H, Cl, NO_2 = 1, 3, 2$) and 100 grams of water at 25°.

Pipetted off 36.256 grams of solution which required 15.10 cc. of 0.0432 normal potassium hydroxide for neutralisation.

Main product 92.4%; byproduct 7.6%.

2. Weighed 364.1 mgrs. of nitration product; shaken with about 100 mgrs. of byproduct and 100 grams of water at 25°.

Pipetted off 69.464 grams which required 27.85 cc. of the said alkali for neutralisation.

Main product 92.8%; byproduct 7.2%.

II. Nitration of *m*-chlorobenzoic acid at -30°; 5 grams treated with 30 grams of absolute nitric acid.

Molecular weight of the nitration product 200.4.

1. Weighed 351.7 mgrs. of the product; shaken with about 100 mgrs. of byproduct and 100 grams of water at 25°. Pipetted off 34.538 grams of solution which required 13.5 cc. of the above alkali for neutralisation.

Main product 93.5%; byproduct 6.5%.

2. 372.8 mgrs. treated as directed; Pipetted off 35.448 grams of solution which required 14.51 cc. of alkali for neutralisation.

Main product 92.8%; byproduct 7.2%.

III. Nitration of *m*-bromobenzoic acid at 0°.

5 grams treated with 30 grams of absolute nitric acid.

Mol. weight of the nitration product 243.7.

Weighed 424.0 mgrs. of the product; shaken with 100 mgrs. or byproduct and 100 grams of water at 25°. Pipetted off 33.945 grams which required 12.19 cc. of alkali for neutralisation.

Main product 88.3%; byproduct 11.7%.

IV. Nitration of *m*-bromobenzoic acid at -30°.

Mol. weight 243.4.

374.4 mgrs. treated as directed. Pipetted off 31.661 grams of liquid which required 9.91 cc. of alkali for neutralisation.

Main product 88.6%; byproduct 11.4%.

Mr. POLAK has repeated these investigations with great care in which he used material prepared by himself. In order to be sure that the nitration products did not retain any nitric acid they were analysed in the manner described, after the test with diphenylamine had become negative. The remainder of the preparation was then again triturated and washed with cold water; the dissolved organic acids were recovered from the washings and the preparation thus purified was again submitted to analysis. The two analyses are indicated with I and II.

Cl 0°. M.W. 202.9 (201.5).

I	0.3374 gr. of nit. mixture } +100 mgr. of z in 100 cc. }	94.333 gr. of sol. β 0.3104	16.39 cc. of (0.0922) <i>n</i> alkali β 92.9%	Tot. sol. 0.328 z 8.0%
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II	0.3315 gr. of nit. mixture } +100 mgr. of z in 100 cc. }	45.516 gr. of sol. β 0.3053	7.28 cc. of (0.0922) <i>n</i> alkali β 92.1%	Tot. sol. 0.3180 z = 7.9%
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Cl-30° M.W. 203.8 (201.5).

I	0.3410 gr. of } nitr. mixture }	98.157 gr. of sol. β : 0.3181	17.43 cc. of (0.0922) <i>n</i> alkali β = 93.3%	Tot. sol. 0.3300 z : 6.7%
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II	0.3275 gr. of } nitr. mixture }	66.284 gr. of sol. β 0.3068	11.40 cc. of (0.0922) <i>n</i> alkali β = 93.7%	Tot. sol. 0.3195 z : 6.3%
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Br 0° M.W. 245.7 (246).

I	0.3320 gr. of } nitr. mixture }	55.477 gr. of sol. β 0.2898	7.32 cc. of (0.0922) <i>n</i> alkali β = 87.0%	Tot. sol. 0.2998 z : 13.0%
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II	0.3292 gr. of } nitr. mixture }	67.915 gr. of sol. β 0.2868	8.96 cc. of (0.0922) <i>n</i> alkali β = 87.1%	Tot. sol. 0.2971 z = 12.9%
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Br. -30°. M.W. 245.2 (246).

I	0.4585 gr. of } nitr. mixture }	89.965 gr. of sol. β = 0.4096	16.48 cc. of (0.0922) <i>n</i> alkali β : 89.3%	Tot. sol. 0.4155 z : 10.7%
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II	0.4385 gr. of } nitr. mixture }	64.190 gr. of sol. β : 0.3192	11.20 cc. of (0.0922) <i>n</i> alkali β : 89.2%	Tot. sol. 0.3957 z : 10.8%
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Let us now include all the figures obtained in the subjoined tables.

I. Nitration of *m*-chlorobenzoic acid; % of byproduct in the nitration mixture.

	DE LEEUW			POLAK			HOLLEMAN, R.20,206		
	%	mol. weight		%	mol. weight		%	mol. weight	
Temp. 0°.	7.6	7.2	203.2	8.0	7.9	202.9	8.7	202.5	calculated
Temp.—30°.	6.5	7.2	200.4	6.7	6.3	203.8	8.3	201.5	201.5

II. Nitration of *m*-bromobenzoic acid.

Temp. 0°.	11.7	243.7	13.0	12.9	245.7	11.4	245	mol. weight calculated
Temp.—30°.	11.4	243.4	10.7	10.8	245.2	11.8	243.2	246

My own figures were deduced from solidifying point determinations.

As regards the titration figures of Messrs. DE LEEUW and POLAK it must be observed that the end reaction was obtained within one drop of $n/10$ alkali so that there can be only a doubt as to one drop more or less. This represents $\frac{1}{200}$ millimol. or about 0.3 % of the quantity taken for analysis. If we consider further that the above figures are deduced from the tables communicated above, the figures of which present inaccuracies of the same order, the difference between the above percentages may be about 0.6 without exceeding the errors inherent to the process.

From this point of view Mr. POLAK's figures may be pronounced excellent ones. It appears from the table that when the molecular weights found approach more closely to the calculated ones, the percentage of the byproducts is higher. This is easy of explanation. For the nitration product may be considered all the purer when there exists a closer agreement between the calculated molecular weight and that actually found. As, however, the impurities are dissolved on shaking with water, and count as main product in the titration, the figures of this become too high and those of the by-products consequently too low.

For this reason the following percentages, showing the composition of the nitration products, must be considered as being nearest to the truth.

I. Nitration of <i>m</i> -chlorobenzoic acid			II. Nitration of <i>m</i> -bromobenzoic acid		
	byprod.	mean prod.		byprod.	main prod.
Temp. 0°.	8	92	Temp. 0°.	13	87
Temp.—30°.	7	93	Temp.—30°.	11	89

The uncertainty of the figures obtained from the solidifying point determinations is a little greater, owing to the circumstance that the mass darkens during the fusion, which causes the solidifying points (which are rather high) to be determined with less sharpness than is usually the case.

August 1908.

Amsterdam, Org. chem lab. University.

Botany. — “*Contribution to the knowledge of the cytological development of *Oenothera Lamarckiana**”, by Mr. J. M. GEERTS. (Communicated by Prof. F. A. F. C. WENT).

(Communicated in the meeting of September 26, 1908).

Among the numerous plants, of which the cytological development has not yet been investigated, *Oenothera Lamarckiana* was the one selected, because a cytological examination of this plant would probably be of importance for the solution of other and more general questions.

Thus it may afterwards perhaps be possible, through a knowledge of the cytology of *Oenothera Lamarckiana* and its mutants, to find an explanation of mutation.

Although the mutation-theory has gained acceptance in most countries, this has not hitherto been the case in England to any considerable extent. There, BATESON and his pupils regard *Oen. Lam.* as a hybrid and attribute the origin of new species to hybrid segregation. The chief argument in favour of this view is that *Oen. Lam.*, like many hybrids, shows a large degree of sterility in the ovules and pollen grains.

In this investigation I therefore set out to trace when and how this sterility arises, in order to be able to judge of the value of BATESON'S argument.

It is quite conceivable that some day we may obtain a full insight into the conditions, through which mutations arise, and also that we may be able to bring about these conditions at will. For this purpose experiments with *Oen. Lam.* are especially desirable, in which attempts should be made to influence the origin of the mutants by subjecting the flowers to various conditions, for instance of temperature, or to various conditions of humidity, to injections etc.

In order to obtain reliable results in such experiments, it is necessary to know exactly, not only which flowers have been subjected to the influence, but also, in which developmental stage the flowers were at the time of treatment, whether before the synapsis, before or after the reducing division etc.; for then only can we determine whether a change in the number of mutants is really the result of the treatment, or is produced by other, unknown causes.

In order to make this investigation available for such experimental investigations, I have therefore also followed out the development of the flower, so as to be able to refer the principal cytological conditions to externally visible stages.

With reference to the mutants and hybrids of *Oen. Lam.* many

questions arise of which the answers may be of importance to cytology itself. Especially hybrids with *O. gigas*, which mutant probably possesses twice as many chromosomes as *Oen. Lam.* itself, might provide material for interesting cytological investigations. For this purpose a knowledge of cytological development of the mutating plant itself is, however, a first desideratum.

The principal results obtained in this investigation, will now be briefly stated.

The floral development of *Oenothera Lamarckiana* was investigated in 1895 by POHL ¹⁾; this author arrived at conclusions, differing widely from those obtained for other *Onagraceae*, for instance by BARCIANU ²⁾ and by PAYER ³⁾, for according to POHL the development is not acropetal, as found by the other investigators. It has now been found, however, that *Oen. Lam.* like other *Onagraceae* has an acropetal development of the flower. In addition the chief points observed in this development, are:

1. The corollar stamen arises from the protuberance, which the corolla forms on its inside.

2. The ovary is the floral axis, which has become hollow. Only the stigmas develop as 4 separate protuberances, alternating with the calyx stamens.

3. The ovary becomes quadrilocular by the growing inwards of 4 parietal septa, which stand before the calyx stamens and fuse in the centre.

4. The axis does not grow further; there is no columella.

5. The placentae are differentiated from the edges of the septa.

6. A corollar stamen and its petal have no common vascular bundle.

7. The ovule arises from periblem and dermatogen, except for the vascular bundle in the raphe.

The cytological development was studied both in the ovules and in the stamens. A summary of the principal phenomena observed, is here appended.

When the mother-cells go into synapsis, the nuclear network contracts, and a thin thread arises, in which chromatin particles can be seen. This thread contracts to a tangle and continually becomes shorter and therefore thicker; this is clearly visible when the tangle unrolls itself

1) Ueber Variationsweite der *Oenothera Lamarckiana* von J. POHL Oosterr. botan. Zeitschrift Jahrgang 1895 Nr. 5 u 6.

2) Untersuchungen ueber die Bluethenentwicklung der *Onagraceae*, Inaug. diss. von D. P. BARCIANU, Naumburg 1874.

3) J. B. PAYER, Organogénie de la Fleur.

again. The thick thread now divides transversely into 14 chromosomes, the nuclear wall disappears, and the chromosomes place themselves perpendicularly to the long axis of the spindle of the heterotypic division. *In the synapsis of Oen. Lam. no double thread can therefore be seen; from that thread the vegetative number of chromosomes is formed, and just before the division these chromosomes show pairing.*

Both in the ovules and in the stamens the synapsis takes place in this manner. In the first division of the mother-cells entire chromosomes separate, which already during this division show a longitudinal splitting for the second division. After this heterotypic division the two nuclei scarcely enter upon a stage of rest, the chromosomes, split longitudinally, always remain visible, especially in the mother-cells of the embryosac. The wall between the two nuclei is often not formed completely. At the second division the halves of the two chromosomes separate, so that 4 nuclei are formed; in general but little staining substance is visible¹⁾.

Whereas in most plants the lowest-cell of the tetrad grows out to form the definitive embryosac, this is not so in *Oen. Lam.* Here the uppermost cell becomes the embryotic, while the other three degenerate; the chromatin of these three cells quits the nucleus, of which the wall disappears, and the chromatin now colours the whole protoplasm dark, so that these three cells of the tetrad remain visible for a long time as a long dark band under the embryosac. In that cell of the tetrad, which grows out, three successive divisions take place in almost all plants, so that 8 nuclei are formed. In *Oenothera* I always found but 4 nuclei, which come to lie in the upper part of the embryosac. A limited number of nuclei is also known in *Helosis guyanensis*, in consequence of the researches of CHODAT and BERNARD²⁾ and in *Mourera*, through an investigation of WEST³⁾. In these plants the lower of the two nuclei, which are formed in the first division, probably degenerates; from the upper nucleus the

¹⁾ In the May meeting of the Dutch Botanical Society, in which I dealt with the greater portion of this subject, I already stated that the synapsis in *Oen. Lam.* takes place in this manner, thereby differing from what has been stated to occur in other plants. As I found in the beginning of September there appeared in the July number of the Botanical Gazette a paper by GATES on the synapsis and reducing divisions in the pollen mother-cells of *Oenothera rubrinervis*. This observer gives much the same succession of stages for the synapsis of this plant.

²⁾ R. CHODAT et C. BERNARD. Sur le sac embryonnaire de *l'Helosis guyanensis*. Journal de Botanique T. XIV, 1900 p. 72.

³⁾ F. A. F. C. WEST. "The development of the ovule embryo-sac and egg in *Podostemaceae*." Recueil des Travaux Botaniques Néerlandais, Volume V, Livraison I, 1908.

three nuclei of the egg-apparatus and the polar nucleus are formed so that division nevertheless takes place three times.

In *Oen. Lam.* I never found a nucleus or remains of a nucleus in the lower part of the embryosac, whilst the four nuclei always lie in the upper portion. A few times it was possible to observe the divisions themselves. Thus I found an embryosac, in which the nucleus was dividing into two, with its spindle in the long axis of the embryosac. Further I found embryosacs with two nuclei, which were sometimes superposed, sometimes side by side. Therefore the lower nucleus probably changes its place, coming to lie higher up in the embryosac. The divisions of these two cells were also found, namely two spindles, in the upper part of the embryosac, and at right angles to each other. In the same manner the spindles are found in most plants above and below in the embryosac, at the third division in couples perpendicular to each other. The division of these two nuclei in *Oen. Lam.* is therefore pretty certainly the last division of the embryosac, in which the two synergids are formed from one nucleus, and the egg-nucleus and the upper polar nucleus from the other. In this particular embryosac, with the two spindles at right angles to each other, there was moreover no trace of nuclei at the chalazal end. We may therefore assume, that in *Oen. Lam.* the first division in the embryosac is suppressed, so that antipodal cells and lower polar nucleus are not formed at all, and that there is not even an antipodal initial cell, which occasionally degenerates again after being formed, as in *Helosis* and *Mourera*.

In the embryo-sac of *Cypripedium* the number of the divisions is still further reduced; here, according to Miss L. PACE¹⁾ there occurs in the embryosac only one homoiotypic division in the lower cell; the upper cell degenerates. The homoiotypic division is not followed by a cell-division. The two nuclei in the lower cell now arrange themselves at the poles; this cell grows out longitudinally and the nuclei divide again, so that they are four in number. Further divisions do not take place in the embryosac; the four nuclei become egg cell, synergids and upper polar nucleus.

When in *Oen. Lam.* the four nuclei have been formed the synergids, which lie nearest to the micropyle, surround themselves, like the egg-nucleus, with their own plasma; the upper polar nucleus remains free in the plasma of the embryosac.

The four cells, which have arisen in the pollen mother-cells through the reduction division, grow out regularly to pollen-grains; the method of origin and the structure of the walls probably agrees in

¹⁾ LULA PACE. Fertilization in *Cypripedium*. Botanical Gazette. XLIV. 1907 p. 353.

Oen. Lam. with what R. BEER¹⁾ has described for *Oenothera longiflora*.

When the pollen-grains are almost mature, the generative and the vegetative nucleus are formed by division; the generative nucleus, which is the smaller, and is surrounded by a quantity of plasma, then applies itself to the wall; the vegetative nucleus remains in the middle of the grain. The division of the generative nucleus into two probably takes place in the pollen-tube.

The pollen-tube penetrates through the micropyle and through the nucellar tissue. It seems as if in this place the nucellar tissue already becomes in advance disorganized. Since, when the pollen-tubes penetrate, the synergids are already completely disorganized and stain very deeply, and since in the nucellus, at the spot where the pollen-tube has penetrated, dark coloured remnants are everywhere visible, I have not succeeded in observing the division of the generative nucleus. Fertilisation itself was however clearly observed. A double fertilisation takes place; one nucleus penetrates into the egg-cell and applies itself against the nucleus; the generative nucleus is at that time round, but smaller than the egg-nucleus, although it probably becomes somewhat larger before fusion. The other generative nucleus, which presents the same shape, applies itself to the polar nucleus. The fusion between the polar nucleus and its generative nucleus takes place more rapidly than that of the other generative nucleus with the egg-nucleus. The fertilized polar nucleus now soon divides, so that frequently there are already a number of endosperm nuclei before the egg-nucleus has completely coalesced with the generative nucleus, and before the egg-cell has a wall of its own. The fertilized egg-cell grows out to a short suspensor, and an embryo with distinct octants. Endosperm nuclei then already lie along the whole of the wall of the embryosac. Afterwards this endosperm however again disappears.

In Oenothera Lamarckiana the endosperm is therefore formed from one fertilized polar nucleus.

In mature stamens very many sterile grains are found in the pollen; in young fruits there occur between the developing seeds a fairly large number of ovules, which are not undergoing development. In both cases the sterility arises after the reduction division. Whilst in all embryo-sac mother-cells the reduction division takes place normally, there are still many ovules in which the upper tetrad-cell also degenerates, this degeneration being accompanied by much the same phenomena as occur regularly in the three lower cells of the

¹⁾ On the development of the pollen grain and anther of some Onagraceae, RUDOLF BEER. Beih. zum Bot. Centr. blatt 1905, 19 I.

tetrad. In the pollen mother-cells also the divisions take place regularly, but after 4 tetrad cells have been formed, only two cells, in general, develop properly, the other two only partially, so that from them grains are formed, from which the contents gradually disappear, although the wall is fairly normal in structure.

Since the divisions are normal, the appearance of this sterility need not at all be the result of a hybrid nature. It follows from the literature on sterility, that, besides in hybrids, sterility occurs in many other plants, and that in most hybrids, which have been examined cytologically, sterility was already present in one or both parents. And since an examination of one hundred species showed sterility to be pretty common among *Onagraceae*, we are not, in my opinion, justified in deducing from the sterility of a plant that it is a hybrid. If the above-mentioned objection of BATESON against the mutation-theory is to have value, it will be incumbent upon him to name the presumptive parents of *Oen. Lam.*

In mature ovaries those ovules, which are not destined to develop, may be recognized by their more transparent nucellus, not containing an embryosac. In such ovulus the penetration of a pollen-tube was never observed, whereas this was repeatedly found in the normal ovules of the same section. *It would appear, therefore, that the normal embryosac exerts an attraction on the pollen-tubes.*

By combining the results of the investigation of the ontogenetic, with those of the cytological development, it appears, that *Oen. Lam.* is very suitable for the experiments, referred to in the introduction, because the cytological development of the pollen and of the ovules are sharply separated in point of time. In flowers of 30 mm. the development of the pollen is almost complete, while in the same flowers the development of the mother-cells in the ovule is only beginning. It would therefore be possible to influence the pollen and the ovules separately, and the flowers which should be selected for this purpose, can be easily recognized after a little practice. Should one wish to influence the pollen before the synapsis, then flowers 10—11 m.m. long should be selected, in which the stamens have a length of 3 mm., since the synapsis of the pollen takes place in flowers of 12—13 mm., in which the anther and also the filament have a length of 4 mm. The synapsis of the embryosac mother-cell takes place in flowers of about $3\frac{1}{2}$ cm. In order to influence this, flowers of $3-3\frac{1}{2}$ cm. should therefore be selected, in which the ovary and the calyx tube have about the same length i.e. $4\frac{1}{2}$ mm.

I hope soon to be able to publish a more detailed description, with plates, of the results of this investigation in the *Recueil des Travaux Botaniques Néerlandais*.

Physiology. — “*About the independence of the electrocardiogram with regard to the form-cardiogram.*” By A. K. M. NOYONS, assistant in the Physiol. Lab. at Utrecht. (Communicated by Prof. H. ZWAARDEMAKER).

Principally by the investigations of ENGELMANN¹⁾ and MARCHAND²⁾ the electromotive phenomena which show themselves in every contracting heart and which we now register in the electrocardiogram, have been reduced to manifestations of the changed current of action that can be produced in every muscular tissue by direct or indirect stimulation of the muscular elements.

Contraction being usually considered as the only visible manifestation of muscular stimulation and action, the electric phenomenon is involuntarily thought to be connected with the process of contraction. On theoretical grounds, however, BIEDERMANN³⁾ deemed it quite possible, “*dasz eine Muskelstelle erregt ist und daher sich negativ zu benachbarten, ruhenden Stellen verhält, ohne dabei in merklichem Grade contrahirt zu sein.*” In these theoretical considerations lies the nucleus of my investigations. Now the experiment teaches that these conceptions are in accordance with reality.

Already in my dissertation⁴⁾ I have, in consequence of some experiments, pronounced the supposition that the electric phenomenon in the contracting heart represents a process by itself, which is borne out by the following experiments.

The heart of an *Anodonta fluviatilis*, laid bare, is in its natural position by means of the unpolarizable magazine-electrodes conducted to the string-galvanometer. (The electrodes with their cottonseeds have previously been put in fresh water for a quarter of an hour and subsequently in the pericard-liquor of the mussel).

The string-galvanometer of EINTHOVEN with permanent magnet (EDELMAANN'S small model) is fed by a current of 4 volt with moderate string-tension (38 out of 60 dividing lines). The movements of the heart are registered by a little lever with a small fulcrum and by a bit of straw placed vertically on the axis, which throws a silhouette on the chink of the registering apparatus. The registration takes place by means of photography.

As appears from the first half of fig. 1 the heart shows regular contractions, attended by electric oscillations, which begin a little earlier.

1) ENGELMANN, PFLÜGER'S Archiv, Bd. XVII, 1878.

2) MARCHAND, PFLÜGER'S Archiv, Bd. XVI 1877 and XVII 1878.

3) BIEDERMANN W., *Elektrophysiologie*, Jena 1895, page 322.

4) NOYONS A. K. M. *Proefschrift: Over den autotonus der spieren*, Utrecht 1908

The cross indicates the place where 3 gtt. of a 3% KCl-solution are dripped upon the heart, which after some time causes a stopping of the form-cardiogram, while the electric phenomenon is altered. Shortly after the KCl-application some feeble movements of the heart are still perceptible in the lever, but they soon stop, whilst the electric fluctuations, which in the beginning of the chemical stimulation-process had become slight, have now nearly reached their original size again.

In fig. 2 the stopping of the heart is seen, while the electrocardiogram remains.

With another trial-object (*Anodonta fluviatilis*), besides those described, also other peculiarities were observed. When by the action of the chemical materials the heart had stopped, the electric phenomenon with the usual frequency of the heart-contractions every time continued manifesting itself periodically. But besides this periodicity it was also clearly observed that in these rhythmic electric phenomena mutually other group-formations appeared, which possessed about the same duration as the periodic length-fluctuations of the autotonus, which, before the stopping of the form-cardiogram, had already been clearly perceptible also in the form-cardiogram.

Also with other animals I had an opportunity to collect data for the independence of the electrocardiogram of the form-cardiogram. The following experiment proves this beyond the possibility of doubt in the heart of *Tripodonotus natrix* under digitonine-poisoning. The heart of a ringed snake was prepared in the afternoon of May 29th. After laying it bare and tying off the veins, the heart was cut out and fixed upon a cork-plate, while the heart-basis and ventricle-point were conducted to the string-galvanometer as described above. The movements of the atrium and ventricle were registered according to suspension-method. Fig. 3 gives the photographic registration of the form-cardiogram and electrocardiogram in the unpoisoned heart.

That same afternoon 5 gtt. of 1% digitonine dissolved in 0.9% NaCl having been added to the heart, we see after some time the typical phenomena of the digitonine-intoxication appear. The next day the heart shows no more alterations in form, unless by means of some expedients (washing with 0.9% NaCl and dripping on of 5 gtt. of CaCl 1% and 3 gtt. of KCl 3%). At 11.30 p m. the heart stands quite still. Notwithstanding this the electric phenomenon quietly continues rhythmically. This state lasts till May 31st. Constantly the electrocardiogram shows the usual spontaneous rhythm. Now 1% digitonine is anew and abundantly dripped upon the heart, which causes a marked effect upon the electric phenomenon. This effect

resembles in its form wellnigh exactly the electric alterations of the electrocardiogram, which already some days before were brought about by dripping the same material upon the heart. See fig. 4.

That the deviation of the string under the influence of the poisoning with digitonine is not a consequence of mechanical or chemical changes in the contact-places of the electrodes, was taught me by repeatedly dripping the electrodes, when the heart was quite dead, while the string-deviation did not take place.

All through that day the regular, periodical electric fluctuations continue though they constantly diminish in size.

It appears that by radiating heat or by cooling down, the frequency and the size of these fluctuations can be respectively increased and decreased, without anything suggesting change of form in the heart being observed. On June 1st the heart stands completely still, also in an electric respect. It only appears that in communication with the galvanometer the heart shows for the first time a strong demarcation-current, proving that it is now partly dead.

Also with a frog's heart I often had an opportunity to observe that the electrocardiogram remains observable after digitalis-intoxication, while the heart shows no change of form. Nor may for this remaining electrocardiogram "fibrillaire Zuckungen", as muscular action, be held responsible, because also when observed with a strong magnifying glass, these movements did not appear visible, while nevertheless the heart quietly continued pulsating electrically.

This peculiar state under digitalis-intoxication is reached best and most certainly, if the heart is not poisoned by administering a larger dose at one time, but by repeatedly dripping new small doses during the whole process of poisoning. In this way I once succeeded in calling forth at a stoppage of the changes of form an electric phenomenon, which for a long time remained larger than the normal electrocardiogram before the poisoning.

If in this way, the poisoning fractioned, takes place with small doses; it may occur that the initial diminution of the electrocardiogram under the influence of the intoxication is at its appearance slackened to a considerable extent. On the whole the above mentioned digitalis intoxication-phenomena in the electrocardiogram may be brought about without differences worth mentioning, both by applying digitaleine and digitonine.

Of one of these poisoning-experiments there follows here a short account. In a *Rana temporaria*, of which cerebrum and spinal marrow have been destroyed by a pique, atrium and ventricle are suspended according to the suspension-method, and basis and apex

cordis are conducted by means of unpolarizable electrodes to the string-galvanometer with permanent magnet. The string-galvanometer is fed with 4 volt.; the string-tension is considerable and amounts to 7 out of the 60 lines of division.

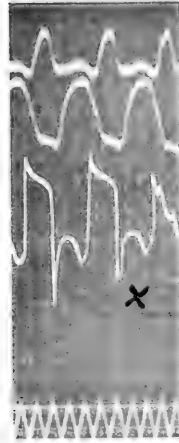
The heart pulsates quietly and vigorously. Some seconds after the beginning of the registration 3 gutturæ of a 1 % solution of digitaleine in 0.9 % Na Cl are dripped on the heart. At once the heart begins to react on this with a slight acceleration in its pulsation whilst the tonus of atrium and ventricle decrease, but shortly after increase considerably. The electrocardiogram, first becoming smaller, soon increases considerably in size, while the rest-position of the string in the interval of the heart-contraction moves to one side. This is shown by fig. 5. Every second minute the dripping with digitaleine is repeated, without every time causing anew the electric changes mentioned. Gradually the contractions of atrium and ventricle grow smaller, whilst the tonus of both increases considerably. A quarter of an hour after the first poisoning the heart stands completely still in systole, as appears from the registration and from the examination of the heart. The electrocardiogram quietly continues pulsating and shows large and small interchanging fluctuations, as is seen in fig. 6. After the lapse of five minutes also the electrocardic pulsations grow smaller and half an hour after the first poisoning they have entirely stopped. Also FANO and FAYOD¹⁾ make mention of electric changes in the heart of *Emys*, stopping under digitalis-poisoning.

Finally we may mention as a proof for the independence of the electrocardiogram the total incongruity between the electric phenomenon and the form-cardiogram, as it appears in the treatment of the heart only, or of the whole trial-animal with toxic materials, though it be in this case impossible to bring about a complete rest of atrium and ventricle. Similar incongruities show themselves e. g. in dripping the heart with antiarine, nitras strychnini, sulfas atropini; by injecting nitras strychnini, sulfas atropini and coffëinum into the veins of the trial-animal; further by exposing the animal in toto to vapours of chloroform, ether and acetic acid.

It is not only the whole heart that shows these incongruities and the peculiar, more or less typical reactions on the applied materials, but also separate parts of the heart may offer such phenomena, as appeared to me when examining the cut-out ventricle of the heart of an eel under the application of antiarine and digitaleine.

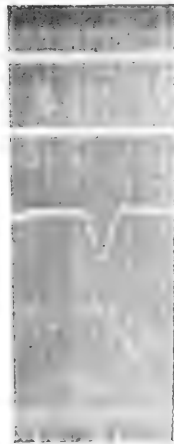
¹⁾ FANO et FAYOD. De quelques rapports entre les propriétés électriques des oreillettes du coeur. *Archiv. ital. de Biologie* Tome IX 1888.

Formcardiogra



The highest graph
ventricle; the tl
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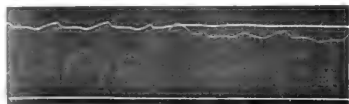
Stopping of



The highest grap
ventricle; the
in half second.

Fig. 1

Form-cardiogram and electrocardiogram of *Anodonta fluviatilis* at KCl-application



The highest line gives the formcardiogram, the next the electrocardiogram, while the third line serves as zero-line; the movement of the registration-plane was 0.22 cm. a second. At the cross the KCl-application takes place.

Fig. 2

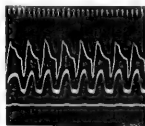
Form cardiogram and electro-cardiogram of *Anodonta fluviatilis* after KCl-application.



The highest line gives the formcardiogram, the next the electrocardiogram, while the third line serves as zero-line; the change of place amounts to 0.22 cm. a second.

Fig. 3.

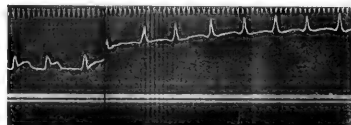
Form-cardiogram and electrocardiogram of the unpoisoned heart of *Tripodonotus matrix*.



The highest line denotes the time in half seconds; then follows the electrocardiogram, the third curved line denotes the contraction of the ventricles; the fourth line the contraction of one of the atria.

Fig. 4.

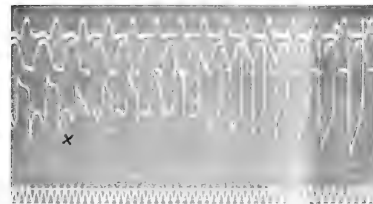
Electrocardiogram of *Tripodonotus matrix* without change of form of the heart. Poisoning process with 1% Digitonine in 0.9% NaCl



The highest lines denotes the time; then follows the electrocardiogram and the two other lines give the graphics of ventricle and atrium. Digitonine application takes place at the cross.

Fig. 5.

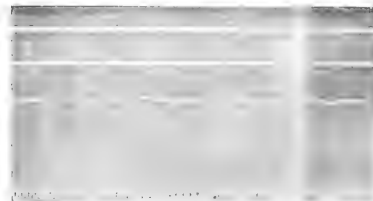
Formcardiogram and electrocardiogram of *Rana temporaria* under application of Digitonine 1%



The highest graphic denotes the formline of the atrium, the next that of the ventricle, the third line indicates the electrocardiogram. The cross denotes the moment of the first poisoning.

Fig. 6.

Stopping of formcardiogram with continuing electrocardiogram 15 minutes after first poisoning



The highest graphic denotes the formline of the atrium, the next that of the ventricle, the third line indicates the electrocardiogram; the time is given in half second.

From what is said above we may conclude not only that in the spontaneously pulsating heart there appear still other actions than those which we find expressed in the contraction, but also that these actions are to some extent independent. The actions not visible to the eye and characterized by definite electric phenomena, suggest the results of stimulation-processes as they can be shown also in the nerve without accompanying change of form. Though, however, the electrocardiogram may possess a certain independence of the form-cardiogram, the above communication does not in the least afford a reason to conversely come to the conclusion of the independence of the latter with respect to the former.

Mathematics. — “*On groups of polyhedra with diagonal planes, derived from polytopes*”. By Prof. P. H. SCHOUTE.

Introduction.

1. By “diagonal plane” of a polyhedron we understand any plane having only edges in common with the boundary of that body.¹⁾

There are two regular polyhedra admitting diagonal planes, the octahedron and the icosahedron. Through any edge of the octahedron passes one diagonal plane, containing the centre and bisecting the dihedral angle of the two faces passing through the edge. Through any edge of the icosahedron pass two diagonal planes; the angle formed by these planes and that formed by the two faces through the edge have the bisecting planes in common, and the cross-ratio between the couple of diagonal planes and the couple of faces has $\frac{1}{2}(3 - \sqrt{5})$ for one of its six mutually connected values.

The fact that only the two mentioned regular bodies possess diagonal planes is closely connected with this that through each of the vertices pass more than three faces. If we take away from the triangular faces meeting in a vertex the sides passing through that vertex, so as to retain of each the side opposite to this vertex, we find in the case of the octahedron a square adjacent to this vertex, in the case

¹⁾ In the last memoir of Dr. FR. SCHUN with the title “Over de meetkundige plaats, etc.” (On the locus of the points in the plane, the sum of the distances of which to n given straight lines is constant, and analogous problems in space of three and more dimensions, *Verhandelingen Kon. Akademie Amsterdam*, first section volume IX, no. 5, 1908) occurs a series of polyhedra with the property that through any edge passes one diagonal plane. By extension to polydimensional spaces polytopes with diagonal spaces also make their appearance.

of the icosahedron a regular pentagon adjacent to this vertex, situated in a diagonal plane. Through any edge AB of the icosahedron pass two diagonal planes, as AB lies in two faces ABP and ABQ and therefore also in the diagonal planes corresponding to P, Q . Through any edge AB of the octahedron passes only one diagonal plane, as the third vertices P, Q of the faces ABP, ABQ through AB are opposite vertices and those points lead here to the same diagonal plane.

The diagonal planes of the icosahedron include a regular dodecahedron.

2. By "diagonal space" of a fourdimensional polytope we understand any space having only faces in common with the boundary of that polytope.

There are two regular cells admitting diagonal spaces, the C_{16} and the C_{600} . Through any face of the C_{16} passes one diagonal space, containing the centre and bisecting the dispatial angle of the two limiting bodies passing through the face. Through any face of the C_{600} pass two diagonal spaces; the angle formed by these spaces and that formed by the two limiting spaces through the face have the bisecting spaces in common, and the cross-ratio between the couple of diagonal spaces and the couple of limiting spaces has again — as we will prove afterwards — $\frac{1}{2}(3 - \sqrt{5})$ for one of its six mutually connected values.

The fact that only the two mentioned regular cells possess diagonal spaces is again closely connected with this that through each of the vertices pass more than four limiting spaces and — we are obliged to add here — that these limiting spaces are tetrahedra⁴⁾. If we take away from the limiting tetrahedra meeting in a vertex the faces passing through that vertex, so as to retain of each the face opposite to this vertex, we find in the case of the C_{16} a regular

⁴⁾ This addition is necessary here. For the spatial sections of the regular C_{24} do not admit diagonal planes, though any vertex of this cell is situated in *six* of its limiting octahedra. As Mrs. A. BOOLE-STOTT pointed out to me these spatial sections admit what we may call "would-be diagonal planes." If we consider — see fig. 64 of vol II of my "*Mehrdimensionale Geometrie*" — of the six octahedra meeting in A the squares adjacent to A , we get the six faces of a cube, the vertices and the edges of which are vertices and edges of C_{24} , whilst the faces of it are not faces of C_{24} . If C_{24} is cut by a space intersecting this cube, the vertices of the section which are points of intersection with edges of the cube will lie in a plane without all the sides of the polygon of intersection with these points as vertices being edges of the section. In the fourth part of my communication "On fourdimensional nets and their sections by spaces" I hope to be able to come back to this point.

octahedron adjacent to this vertex, in the case of the C_{600} a regular icosahedron adjacent to this vertex, situated in a diagonal space. Through any face ABC of the C_{600} pass two diagonal spaces, as ABC lies in two spaces $ABCP$, $ABCQ$ and therefore also in the diagonal spaces corresponding to P , Q . Through any face ABC of the C_{120} passes only one diagonal space, as the fourth vertices P , Q of the limiting spaces $ABCP$, $ABCQ$ through ABC are opposite vertices and these points lead here to the same diagonal space.

The diagonal spaces of the C_{600} include a regular C_{120} .

3. By "diagonal space Sp_{n-1} " of an n -dimensional polytope we understand any space Sp_{n-1} having with the boundary of this polytope only limiting spaces Sp_{n-2} in common.

Of the three regular polytopes, the simplex $S_{(n+1)}$ with $n+1$ vertices and $n+1$ limiting spaces Sp_{n-1} , the measure polytope M_n with 2^n vertices and $2n$ limiting spaces Sp_{n-1} , and the cross polytope Cr_n with reversely $2n$ vertices and 2^n limiting spaces Sp_{n-1} , only the last one possesses diagonal spaces Sp_{n-1} . Through any space Sp_{n-2} bearing a limiting simplex $S_{(n-1)}$ passes one diagonal space Sp_{n-1} , containing the centre and bisecting the angle between the two limiting spaces Sp_{n-1} passing through this Sp_{n-2} .

The fact that of the three regular polytopes only the cross polytope possesses diagonal spaces Sp_{n-1} is once more closely connected with this that through each of the vertices pass 2^{n-1} — and therefore more than n — limiting spaces Sp_{n-1} . If we take away from the limiting simplexes $S_{(n)}$ passing through any vertex the spaces Sp_{n-2} passing through this vertex, so as to retain the 2^{n-2} spaces Sp_{n-2} opposite to this vertex, we find the cross polytope Cr_{n-1} adjacent to this vertex, situated in a diagonal space Sp_{n-1} . Here too through any space Sp_{n-2} containing a limiting simplex $S_{(n-1)}$ pass two limiting spaces Sp_{n-1} . But, as the new vertices P and Q of the simplexes $S_{(n)}$ situated in these limiting spaces are opposite vertices of Cr_n leading to the same Cr_{n-1} , through each limiting simplex $S_{(n-1)}$ passes only one diagonal space Sp_{n-1} .

4. By intersecting a fourdimensional polytope, each face of which is situated in d diagonal spaces, by a space not containing an edge of the polytope, we get as section a polyhedron with the property that each of its edges is contained in d diagonal planes. For, if the intersecting space meets a face of the polytope, it meets also the d diagonal spaces passing through that face, and this always furnishes an edge of the section and d diagonal planes passing through it. So

the sections of the cells C_{16} and C_{600} by an arbitrarily chosen space are polyhedra with the property that through each edge passes respectively one diagonal plane or a couple of these. As four spaces passing in Sp_4 through the same face are cut by any space of Sp_4 in four planes through a line with the same cross-ratio, the sections of C_{600} by a space not containing an edge will be characterized by the property that the couples of faces and diagonal planes through an edge possess a constant cross-ratio. For from the regularity of C_{600} can be deduced that this cross-ratio is the same for all the faces, as we have stated already. Now the section of C_{600} by a space normal to an axis OE_0 (through a vertex E_0) is a regular icosahedron, if only the intersecting space is quite close to E_0 and this proves that the constant cross-ratio of C_{600} must be equal to that of the icosahedron.

5. Indeed, it is not difficult to show directly that the cross-ratio of C_{600} is really $\frac{1}{2}(3 - \sqrt{5})$.

Let ABC be any face of C_{600} and O, P, Q (fig. 1) represent successively the centre of C_{600} and the fourth vertices of the two limiting tetrahedra $ABCP, ABCQ$ passing through ABC . Then the plane OPQ of the diagram will contain the centre of gravity G of the face ABC and be perfectly normal to this face in this point. From $GP=GQ$ and $OP=OQ$ can be deduced that the quadrangle $OPGQ$ is a deltoid with OG as axis of symmetry. As furthermore the normals GP' and GQ' dropped from G on OP and OQ are the traces of the plane of the diagram with the two diagonal spaces, we get for the cross-ratio ($PQRS$)

$$\frac{PR}{PS} : \frac{QR}{QS} = \left(\frac{PR}{PS}\right)^2 = \left(\frac{\tan \alpha - \tan \beta}{\tan \alpha + \tan \beta}\right)^2 = \frac{\sin^2(\alpha - \beta)}{\sin^2(\alpha + \beta)}.$$

Now if the edge of C_{600} is our unit and we represent for brevity's sake $\sqrt{5}$ by e we have (see my "*Mehrdimensionale Geometrie*", vol. II, p. 200)

$$OP = \frac{1}{2}(e + 1), \quad OP' = \frac{1}{4}(e + 3), \quad OG = \frac{1}{6}(e + 3)\sqrt{3}, \quad PG = \frac{1}{3}\sqrt{6}.$$

From this ensues

$$\beta = 60^\circ, \quad \sin \alpha = \frac{1}{8}(e + 1)\sqrt{6}, \quad \cos \alpha = \frac{1}{4}\sqrt{7 - 3e}$$

and therefore

$$(PQRS) = \left(\frac{e-1}{2}\right)^2 = \frac{1}{2}(3-e) = 0,381966 \dots ^1)$$

¹⁾ In the same way the cross-ratio of the four planes through an edge of the icosahedron can be found.

6. In the third part of my communications "On fourdimensional nets and their sections by spaces", which is about to appear in these "Proceedings" we shall find occasion to fix attention on the diagonal planes presenting themselves in the sections of the C_{16} . As any vertex — or rather any couple of opposite vertices — of C_{16} possesses an adjacent octahedron, the polygons situated in these diagonal planes are always sections of octahedra. Probably the diagonal planes presenting themselves in the sections of the C_{600} were discovered for the first time by Mrs. A. BOOLE-STOTT, who made models of these sections, and explained as sections with diagonal spaces by Mr. H. W. CURJEL.¹⁾

The object of this paper is to study more closely the cases in which the intersecting space contains one or more edges of C_{16} and C_{600} ; of the results revealed by these considerations these about C_{600} have especially roused our interest.

A. *The spatial sections through an edge of C_{16} .*

7. We consider the case in which the intersecting space contains the edge AB of C_{16} and indicate by A' and B' the vertices opposite to A and B . Then all the vertices except A and A' are adjacent to A and A' , all the vertices except B and B' are adjacent to B and B' , and so the four other vertices P_1, P_2, P_3, P_4 (fig. 2) are adjacent to A and B at the same time. In other words: the octahedra adjacent to A and B , situated in different spaces, penetrate one another in the square $P_1P_2P_3P_4$, the vertices of which they have in common. So through the edge AB pass two diagonal spaces, one of which corresponds to the opposite vertices P_1, P_3 , the other to the opposite vertices P_2, P_4 ; they intersect the plane of the square $P_1P_2P_3P_4$, perfectly normal in O to the plane through AB and $A'B'$, respectively in the diagonals P_2P_4, P_1P_3 . If l is the trace of the intersecting space through AB on the plane $P_1P_2P_3P_4$, and this line l , determining with AB that space, meets the diagonals P_2P_4, P_1P_3 in the points S_{13}, S_{24} situated within the square, then the section will show the particularity that the planes ABS_{13} and ABS_{24} are diagonal planes; so in some cases the edge AB will lie in *two* diagonal planes.

In the third communication "On fourdimensional nets, etc." quoted above will be indicated that the particularity of an edge being situated

¹⁾ A series of these models, showing e.g. the decomposition of the 120 vertices of the C_{600} into the vertices of five cells C_{24} , has been inserted lately into the collection of mathematical models of the University of Groningen.

in two diagonal planes does not present itself in the four groups of principal sections of C_{16} .

B. *The spatial sections through an edge of C_{600} .*

8. Through any edge AB (fig. 3) of C_{600} pass five limiting tetrahedra of this cell; the five edges opposite to AB of these tetrahedra are the sides of a regular pentagon $P_1P_2 \dots P_5$, the vertices of which are at the same time adjacent to A and B . In other words: the icosahedra adjacent to A and B , situated in different spaces, penetrate one another in the regular pentagon $P_1P_2 \dots P_5$, adjacent to AB , the vertices of which are common to both. So through the edge AB pass five diagonal spaces corresponding respectively to the five vertices P_1, P_2, \dots, P_5 ; they intersect the plane of the pentagon, perfectly normal in its centre M to the plane ABM , in the diagonals $P_5P_2, P_1P_3, \dots, P_4P_1$ of the pentagon, or — if one likes — in the sides of the starpentagon $P_1P_3P_5P_2P_4$. In the case of C_{16} the centre O of the square $P_1P_2P_3P_4$ was at the same time the centre of the cell. Here the centre M of the pentagon is not even the centre of the two icosahedra penetrating one another, and still less the centre of C_{600} ; here the line joining M to the midpoint M' of the edge AB must contain the centre O of C_{600} .

If the trace l of the intersecting space on the plane of the pentagon adjacent to AB cuts P_5P_2 in S_1 (fig. 3), ABS_1 is a diagonal plane. For this plane is the intersection of the intersecting space determined by AB and l with the diagonal space determined by AB and P_5P_2 of the icosahedron adjacent to P_1 , and S_1 lies on P_5P_2 itself, not on its production. Indeed it is evident that this icosahedron is cut by any plane through AB and a point of P_5P_2 , if this point lies on P_5P_2 itself, whilst the plane will contain of this icosahedron the edge AB only, if this point lies on P_5P_2 produced. In order to prove this we have only to observe that the lines AB and P_5P_2 , the first of which is an edge of C_{600} and the latter a chord, cross one another normally. From this it ensues that these lines, likewise edge and chord of the icosahedron determined by the points A, B, P_5, P_2 , can be represented (fig. 4), in projection on a plane through two opposite edges $pr, p'r'$ of the icosahedron, by the edge in q normal to the plane of the diagram and the chord pp' situated in that plane, the extremities of the edge being joined by edges to the extremities p, p' of that chord. This shows immediately that any plane through the edge projecting itself in q cuts the icosahedron or not, according to whether the point of intersection of the plane with pp' lies on this line itself or on its production.

So for the position of the intersecting space adopted in fig. 3 four diagonal planes ABS_1 , ABS_2 , ABS_3 , ABS_4 pass through AB ; the point of intersection S_5 of l and P_4P_1 falls on the production of this side and does not lead to a diagonal plane.

On each side P_5P_2 of the starpentagon (fig. 3) there are remarkable points besides the extremities P_5 , P_2 , which lead to faces and not to diagonal planes, namely the points of intersection Q_3 , Q_4 with the other sides and the midpoint M_1 . If S_1 coincides with Q_3 , the sides P_5P_2 and P_4P_1 are cut in the same point and, the two corresponding diagonal planes coinciding with one another in the plane of intersection of the diagonal spaces ABP_5P_2 and ABP_4P_1 adjacent to P_1 and P_5 , this plane must contain the pentagon adjacent to the edge P_1P_5 of C_{600} . So in this case the polygon situated in the diagonal plane — compare in fig. 4 the planes normal to the plane of the diagram in the lines qr and qr' — is a regular pentagon. If S_1 coincides with M_1 the plane ABM — compare fig. 4 —, being a plane of symmetry of the icosahedron, contains AB and the edge parallel to AB .

9. My second memoir with the title "Regelmässige Schnitte u.s.w." Regular sections and projections of C_{120} and C_{600} . Verhandelingen Amsterdam, first section, vol. IX, N^o. 4, 1907 contains the data that enable us to determine, for any position of the intersecting space containing a certain number of edges of C_{600} belonging to the four groups of sections studied there, the number and the position of the diagonal planes passing through any one of these edges, and to construct the icosahedral sections situated in these planes. We will try to explain this shortly.

On the righthand side of the plates II, IV, VI, VIII has been indicated how the icosahedra adjacent to the vertices of C_{600} project themselves on the axes OR_0 , OP_0 , OK_0 , OE_0 . In order to see at a glance which sections normal to these axes do contain edges of icosahedra — and therefore also of C_{600} — we consult the upper lines of the plates XVIII, XVI, XIV, XII. We find then the following table:

II ^b , XVIII		$a_1(6)$,	$d_1(12)$,	$e_1(12)$,	$f_1(6)$,
IV ^b , XVI		$a_2(3)$,	$e_2(3)$,	$e_3(3)$,	$f_2(6)$, $h_3(6)$, $i_3(3)$,
VI ^b , XIV		$a_3(1)$,	$b_3(5)$,	$c_3(10)$,	$f_3(5)$, $g_3(10)$, $i_3(10)$,
VIII ^b , XII		$b_4(30)$,	$c_4(30)$,	$e_4(60)$,	

in which the indices 1, 2, 3, 4, distinguishing the groups, correspond

to those of the groups of icosahedra on (II^b) , IV^b , VI^b , $VIII^b$, whilst the numbers placed between brackets indicate how many edges lie in the intersecting spaces. However the cases a_1 , a_2 , a_3 can be left out, as referring to intersecting spaces leaving the C_{600} totally on one side and being therefore unable to furnish sections containing diagonal planes; for each of the sixteen remaining cases the trace l of the intersecting space on the plane of the pentagon adjacent to the chosen edge must be constructed. These traces, indicated by the symbols d_1 , e_1, \dots, e_4 of the cases to which they belong, are represented altogether in fig. 5.

10. The determination of the trace l causes the least trouble if this line contains two of the remarkable points P_i , Q_i , M_i corresponding respectively to a vertex, a point of intersection of two non-adjacent sides and the midpoint of a side of the starpentagon. In order to divide the difficulties we treat these simple cases first.

Case d_1 . On plate II^b we find under d that the groups I and VII, each containing four icosahedra, furnish faces situated in the intersecting space, whilst group III gives six icosahedral sections through two opposite edges. So the trace d_1 to be found passes through a vertex P_i and a midpoint M_i ; if P_1 is taken as P_i , then M_i must be either M_3 or M_4 . So we find that the trace d_1 coincides with one out of ten homologous lines, if by "homologous" lines we mean lines passing into one another either by a rotation of the pentagon about its centre M to an amount of any multiple of 72° or by a reflexion with respect to one of the lines MP_i as mirror, i.e. in general by any transformation that transforms the pentagon into itself.

The line d_1 cuts two other sides, the sides P_3P_2 and P_3P_5 , of the starpentagon; as P_1 does not lead to a diagonal plane, any of the 12 edges lying in the intersecting space is contained in three diagonal planes. These new diagonal planes are connected with the groups IV and VI, each of which contains 12 icosahedra. As the section passes rather near the centre M_i in the case of IV and rather near one of the extremities P_i in the case of VI, it is probable that IV corresponds to the point on P_3P_2 , VI to the point on P_3P_5 . Later on we will prove this to be true.

We will add the remark, that the number 12 of the edges lying in the intersecting space is given back by each of the groups I, III, IV, VI, VII, the corresponding diagonal planes — the *faces* of I and VII included — containing successively 3, 2, 1, 1, 3 edges.

Case e_1 . On plate VI^b under e the group I_1 leads to a point Q

and the group Π_3 to a point M_i ; if Q_1 is chosen as Q_i , M_i must coincide either with M_2 or with M_5 .

The chosen line c_3 furnishes one point of intersection more, on P_5P_2 ; so there must be one group of icosahedra more with an edge situated in the intersecting space. Indeed, we find only one group VI_3 , IV_8 belonging again to Q_1 .

Case e_4 . On plate VIII^b under e we have to deal with a central section of C_{600} , from which ensues that the line e_4 passes through the centre M of the pentagon. Moreover the groups III_4 , IV_4 , V_4 furnish successively a point P_i , a point Q_i , a point M_i . So e_4 is a diameter through a vertex of the pentagon, e.g. $P_1M_1Q_1$. Here no other point of intersection appears.

11. It would be possible to go on in this manner and to treat successively, proceeding from the easier cases to the more difficult ones, the remaining lines through two remarkable points, the lines through only one remarkable point, the lines parallel to one of the sides. We prefer however to explain now, for an arbitrary case, how the ratio of division of the side of the starpentagon corresponding to a determined group of icosahedra can be found by means of Fig. 3 of the quoted memoir, which is repeated here with slight modification as fig. 4.

We therefore consider the group IV , of plate II^b mentioned above under d_1 , and remember that the icosahedral sections corresponding to this group are determined, according to the quoted memoir, by planes normal to the plane of fig. 4 in a line parallel to pp^I . If the edge normal in q to the plane of that diagram is once more the edge AB and the chord pp' situated in that plane the side of the starpentagon, then the point S on that side determining the diagonal plane in question is found by drawing through q the line qS parallel to pp^I . Now pw is the smaller segment of the line pp' divided internally in medial section and the same relation holds for $p^{II}r = wq$ with respect to the segments $p^I r = p^{II} s = sq$. So if the ratio of the side of the regular pentagon to its diagonal is indicated by $\frac{s}{d}$, we deduce from similar triangles

$$p^{I}w : wq = pw : wS,$$

which may be transformed into

$$p^I q : p^{I}w = pS : pw.$$

This leads to

$$\frac{pS}{pp'} = \frac{3d + 2s}{3d + s} \cdot \frac{pw}{pp'} = \frac{3d + 2s}{3d + s} \cdot \frac{d - s}{d} = \frac{(2+e)(3-e)}{5+e} = \frac{1+e}{e+5} = \frac{1}{5} e.$$

By this value the place of S on pp' is perfectly determined; however in fig. 5 we may — and, if d_1 has been determined by P_1 and M_3 , we must — assume for S not the point on the right of M_1 corresponding to this ratio but the point on the left.

As a second example we consider the group IX₂ of plate VI^b to which — according to the second memoir — corresponds a series of planes normal to the plane of fig. 4 parallel to up_2^{III} (p_2^{III} being the midpoint of sv). We draw through s and q the lines sS'' and qS' parallel to up_2^{III} and determine now the ratio of pS' to pp' by means of similar triangles as follows. These triangles give

$$\frac{S'w'}{qw'} = \frac{w'S''}{w'w''} = \frac{pS''}{ps} = \frac{pS''}{w'u} = \frac{pw'}{w'u} = \frac{pw'}{\frac{1}{2}qu}.$$

So we have

$$\frac{S'w'}{pp'} = \frac{2qw'}{qu} \cdot \frac{pw'}{pp'} = \frac{2s}{d+s} \cdot \frac{s}{d}$$

and finally

$$\frac{pS'}{pp'} = \frac{pw' - S'w'}{pp'} = \frac{s}{d} \left(1 - \frac{2s}{d+s} \right) = \frac{s(d-s)}{d(d+s)} = \frac{(e-1)(3-e)}{2(e+1)} = \frac{1}{2}(7-3e).$$

In this way is obtained the complete system of the twelve different ratios λ given in the following table, where, when λ differs from $\frac{1}{2}$, the value smaller than $\frac{1}{2}$ always appears. For all the groups in any horizontal row λ has the value indicated in the last column but one. In the last column are given the numbers of centimeters corresponding to these ratios, when the length of the side of the starpentagon (fig. 5) is 20 centimeters. Finally the last column but two indicates the direction of the trace of the intersecting planes normal to the plane of fig. 4, by means of which the values of λ have been calculated. (See table p. 287).

For the sake of clearness the values of λ with the side (20 centimeters) of the starpentagon of fig. 5 as unit have been indicated separately in fig. 6. By transferring this scale division in fig. 5 to each of the sides P_1P_2 , etc. we are enabled to draw immediately each of the traces l in question with accuracy.

12. By means of the preceding the polygon of intersection of the polyhedron situated in any assigned diagonal plane can be constructed. To this end we indicate in fig. 7, which is a repetition of fig. 4, for the twelve different cases of the table by the numbers 1, 2, . . . , 12 the traces of the intersecting planes passing through the edge in q normal to the plane of the diagram, and show how we can obtain all the measures necessary for the construction of these

Nr.	Groups					λ	
1	I ₁ , II ₁ , VII ₁	II ₂ , XI ₂		III ₄	qp	0	0
2	III ₁	I ₂ , VII ₂	II ₃ , V ₃	V ₄	qO	$\frac{1}{2}$	10
3			I ₃ , IV ₃ , IX ₃	II ₄ , IV ₄	qs	$\frac{1}{2}(3-e)$	7.63932
4	IV ₁		VIII ₃		pp^I	$\frac{1}{5}e$	8.94427
5	V ₁	IV ₂			pp^{II}	$2(e-2)$	9.44272
6	VI ₁		III ₃		pp^{III}	$e-2$	4.72136
7	VIII ₁	V ₂			pp^{IV}	$\frac{1}{4}(e-1)$	6.18034
8		VI ₂			pp_2^{II}	$\frac{1}{6}(5-e)$	9.14207
9		IX ₂			up_2^{III}	$\frac{1}{2}(7-3e)$	2.91736
10		X ₂	VI ₃		qp_2^{IV}	$\frac{1}{10}(5-e)$	5.52786
11		XI ₂			Op^{IV}	$\frac{1}{4}(3e-5)$	8.54102
12			IX ₃		Or	$\frac{1}{4}(3-e)$	3.81966

polygons represented in fig. 8 by laying down in the plane of the diagram of fig. 7 the regular pentagon projecting itself in psv and the equilateral triangle projecting itself in rv . By the remark that all these polygons admit an axis of symmetry, the line k bisecting the edge q_1q_2 normally, and that the measures qab , aa' of the pentagon of Nr. 9 and $qcde$, dl' , ee' of the octagon of Nr. 4 used in fig. 8 are taken from fig. 7 this construction will become sufficiently clear. ¹⁾

We add to this the following simple general remark. The polygon situated in a diagonal plane of which one of the sides is an edge of C_{600} is always either a pentagon, or a hexagon, or an octagon. If we once more determine the diagonal plane by means of the edge normal in q to the plane of fig. 4 and the point of intersection S with pp' , then the section is a pentagon if S lies between p and

¹⁾ The letters a and c , that had to indicate points on k , have been omitted in fig. 8.

w or between w and p' and an octagon if S lies between w and w' , except when S coincides with the midpoint in which case the section is a hexagon. In other words, with reference to the side $P_5 P_2$ of the starpentagon of fig. 5: the section is a hexagon if S coincides with M_1 , an octagon if S lies elsewhere between Q_3 and Q_4 , a pentagon if S falls between P_5 and Q_3 or Q_4 and P_2 . So in the case h_2 we find two pentagons, since two points of intersection lie outside the pentagon with the vertices Q_i , a hexagon and an octagon, etc.

13. The method developed here has a slight drawback, revealing itself to the utmost in the determination of the exact position of the trace h_2 . The difficulty consists in this that the method leaves us in the dark as to the succession of the different values of λ on the trace l . If we have deduced that the different ratios of VI_2 , VII_2 , IX_2 , X_2 present themselves and we have chosen for VII_2 the centre M_3 (fig. 5) we are obliged to investigate by a rotation of the ruler about M_3 on which side — and in which of the two different points on this side — we must assume the point of division corresponding to VI_2 in order to make the other points of intersection to correspond to IX_2 and X_2 . We now indicate finally how this difficulty can be overcome.

To any chosen edge of C_{600} projecting itself on plate IV^b in h on the axis OF_0 , there correspond five adjacent points of C_{600} . If now it were possible:

1. to select a determined edge projecting itself in h on OF_0 ,
2. to point out the five adjacent vertices and to indicate in what order these points are the vertices of a regular starpentagon,
3. to find where these five points project themselves on the same axis OF_0 ,

then it would be possible to make out, in what ratio the successive sides of the starpentagon were divided in projection on OF_0 by h , which would enable us to fix in fig. 5 on each of these sides a quite definite point. Really in these suppositions the difficulty would be quite dissolved.

Now these suppositions are quite realisable, by means of the tables published in my first memoir with the title "Regelmässige Schmitte u. s. w." (Regular sections and projections of C_{120} and C_{600} , Verhandelingen Amsterdam, first section, vol. II, No. 7, 1894); we will explain this with the aid of fig. 9 for the case of the trace h_2 .

1, 24)

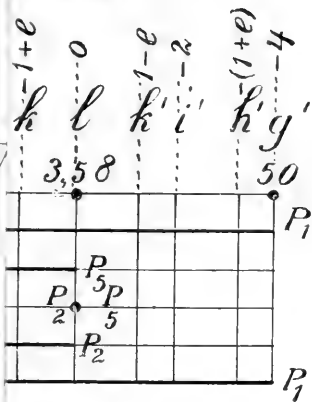


Fig. 10

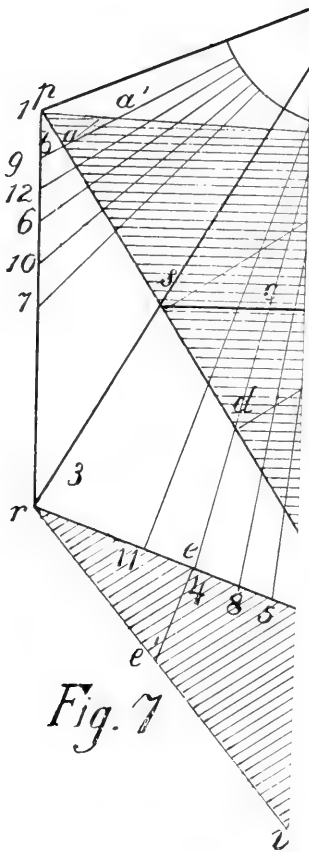
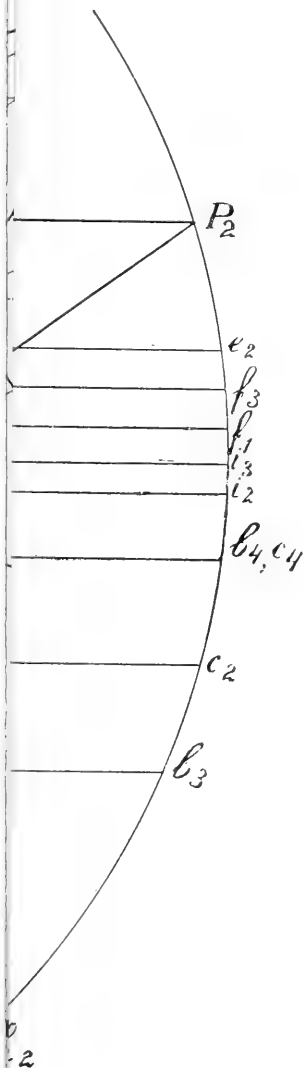


Fig. 7

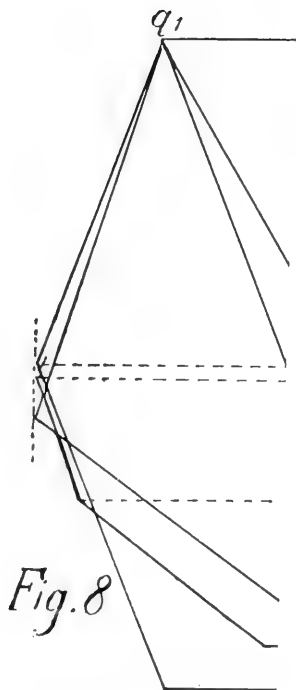
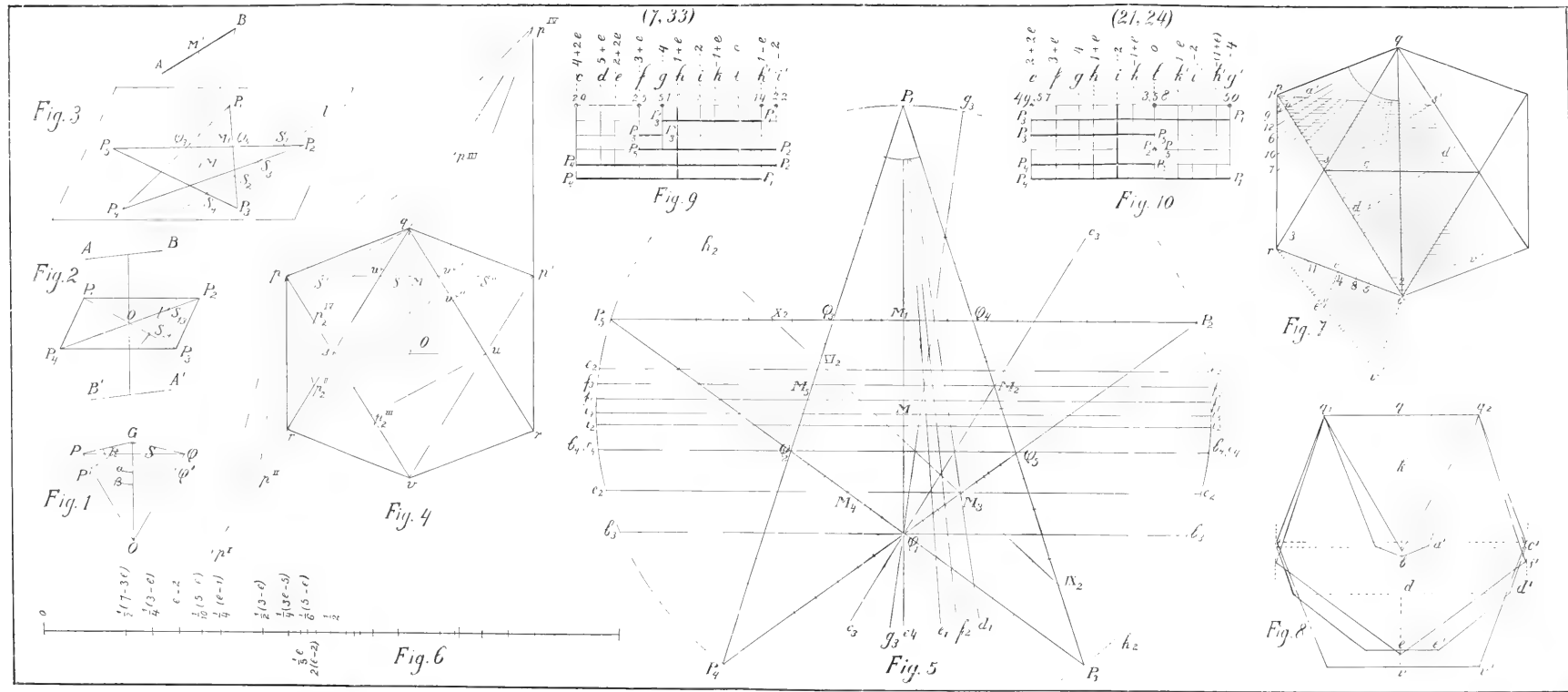


Fig. 8



14. In "Tabelle I" with the inscription "Coordinatenstellung des Z^{000} " we find, if under "C, Zweite Querlinie" the z_1 corresponds to the chosen axis OP'_0 , that the vertices

$$-6, 7, -11, -12, 17, -18, 19, 20, 33, -34, 35, 36$$

have $1 + e$ for value of z_1 and project themselves therefore in h — compare plate IV^b of the second memoir. From "Tabelle II" with the inscription "Kanten des Z^{000} " we then deduce that (7,33) is an edge of C^{000} , that 14, 22, 25, 29, 51 are the five vertices adjacent to this edge (7,33) and these points form a regular pentagon $P_1P_2P_3P_4P_5$ in the order of succession 14, 22, 51, 29, 25 and therefore a regular starpentagon $P_1P_3P_5P_2P_4$ in the order 14, 51, 25, 22, 29. Turning back to the column z_1 of "Tabelle I" we find at last that these vertices 14, 51, 25, 22, 29 admit successively for z_1 the values

$$1 - e, 4, 3 + e, -2, 2(2 + e),$$

from which ensues that they project themselves — compare again plate IV^b of the second memoir — in k', g, f, i', c . This result is indicated in fig. 9. While the segments of the horizontal lines appearing there from right to left are indicated as to their relative length by

$$d, s, d, d, s, d, s, d, d, s,$$

we find, if we indicate by S the point on any side of the starpentagon projecting itself in h ,

$$\frac{P_3S}{P_3P_1} = \frac{s}{3d + 2s} = \frac{1}{2}(7 - 3e), \quad \frac{P_4S}{P_5P_2} = \frac{d + s}{4d + 3s} = \frac{1}{10}(5 - e),$$

$$\frac{P_4S}{P_4P_2} = \frac{1}{2}, \quad \frac{P_1S}{P_1P_4} = \frac{3d + s}{6d + 3s} = \frac{1}{6}(5 - e).$$

These results are in accordance with what has been found before; moreover they indicate quite definitely the place of each point of division ¹⁾).

15. If we apply the new method to the case of a trace as e_2 parallel to one of the sides of the starpentagon, then the point S projecting itself in e on plate IV^b will have to divide the side P_1P_2 externally into the ratio unity and this requires, as S does not lie at infinity, that the edge P_1P_2 projects itself on OE'_0 as a point.

¹⁾ As the second method gives something more in one respect than the first, it might seem superfluous to communicate the first. We are not of this opinion. For the first method has this advantage above the second that it leads immediately to a construction of the polygon situated in the diagonal plane as the section of a definite icosahedron by a definite plane.

This case is represented in fig. 10 for the edge (21; 24), where 3, 49, 50, 57, 58 are the five adjacent points, whilst 50, 3, 49, 57, 58 appears as the pentagon $P_1P_2P_3P_4P_5$, 50, 49, 58, 3, 57 as the starpentagon $P_1P_3P_5P_2P_4$. Really P_5P_2 projects itself into a point; moreover P_3P_1 and P_4P_1 on one hand and P_4P_3 and P_2P_5 on the other coincide in projection, which is closely connected with this that λ is the same for the two constituents of each pair.

Mathematics. — “On triple systems, particularly those of thirteen elements.” By Dr. J. A. BARRAU. (Communicated by Prof. D. J. KORTEWEG).

(Communicated in the meeting of September 26, 1908).

In a paper to this Academy¹⁾ Prof. J. DE VRIES gave a triple system of 13 elements of a different type than the cyclic system of Prof. NETTO²⁾; he added however the observation, that no proof has been furnished of these types being the only ones.

Mr. K. ZULAUF shows in his dissertation³⁾ that the systems given formerly by KIRKMAN (1853) and REISZ (1859) are identical to that of DE VRIES, so that the number of *known* systems is *two*; neither is anything here decided about the number of *possible* systems.

It seemed desirable to decide upon this point by means of a special investigation⁴⁾. To this end some facility is offered by using those expressions which are used in the theory of the configurations, by regarding the 13 elements as *points*, the 26 triplets as *lines* which bear three of the points; the whole of the triple system then becomes the scheme of a diagonalless Cf. $(13_6, 26_3)$ where it is irrelevant whether this Cf. can be geometrically realized or not. A classification of these Cff. is now our aim in view.

The rest figure of the second order of a line of such a Cf., i.e. what remains if we leave out that line with its three points and the 3×5 lines passing through these points, is of necessity a Cf. (10_3) , the 10 points of which are in three ways perspective and that according to the three points left out.

But then reversely each imaginable Cf. $(13_6, 26_3)$ of the desired type is obtained by:

- 1st. starting from all possible Cf. (10_3) ,
- 2nd. by constructing for each Cf. (10_3) the Cf. $(10_3, 15_2)$ of its diagonals,

1) *Versl. Kon. Akad. v. Wet.* III, p. 64, 1894.

2) *Substitutionentheorie*, p. 220; *Math. Annalen*, Vol. 42.

3) “*Ueber Tripelsysteme von 13 Elementen*”, Giessen, 1897.

4) I subsequently find this question treated also by DE PASQUALE (*Rendic. R. Ist. Lombardo*, 2nd Ser., 32, 1899).

3rd. by investigating for each of these Cff. (10₃, 15₂) in how many ways its 15 lines break up into three *principal five-sides*¹⁾,

4th. by imagining for each of these cases the 5 lines of each principal five-side as converging to one point and these three points as collinear.

The number of types of Cff. (10₃) amounts, according to the classifications of KANTOR²⁾ and SCHROETER³⁾, to *ten*, to be distinguished

Those of the system of KIRKMAN are:

K	1	1	1	2	2	3	3	5	5	7	1	2	3	4	6	1	2	3	4	6	1	2	3	4	5	<i>a</i>	
	2	4	6	4	8	4	9	6	7	8	8	5	7	0	9	9	0	5	7	8	0	7	6	9	8	<i>b</i>	
	3	5	7	6	9	8	0	0	9	0	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	
<hr/>																											
	IX	VIII	V	V	V	V	VIII	V	IX	V	VIII	V	V	II	VIII	VI	VIII	V	VIII	IX	X	III	III	X	III	X	

The Cff. of the diagonals of the 10 Cff. (10₃) are resp.:

	II	III	IV	V	VI	VII	VIII	IX	X
1 8	1 8	1 8	1 8	1 8	1 8	1 8	1 8	1 8	1 8
1 9	1 9	1 9	1 9	1 9	1 9	1 9	1 9	1 9	1 9
1 0	1 0	1 0	1 0	1 0	1 0	1 0	1 0	1 0	1 0
2 5	2 5	2 5	2 6	2 6	2 5	2 5	2 5	2 5	2 5
2 7	2 7	2 6	2 7	2 7	2 7	2 7	2 9	2 6	2 7
2 0	2 0	2 0	2 0	2 0	2 0	2 0	2 0	2 4	2 9
3 4	3 4	3 4	3 4	3 4	3 4	3 4	3 5	3 7	3 5
3 6	3 6	3 7	3 5	3 5	3 6	3 6	3 6	3 8	3 6
3 0	3 0	3 0	3 0	3 9	3 9	3 8	3 7	3 0	3 7
4 7	4 7	4 7	4 7	4 7	4 7	4 7	4 7	4 7	4 7
4 9	4 9	4 9	4 9	4 0	4 9	4 9	4 8	4 9	4 8
5 6	5 6	5 6	5 6	5 6	5 6	5 6	4 9	5 6	4 9
5 9	5 8	5 8	5 8	5 8	5 8	5 0	5 7	5 0	5 0
6 8	6 8	6 9	6 9	6 8	6 8	6 8	6 8	6 8	6 8
7 8	7 9	7 8	7 8	7 9	7 0	7 9	6 0	7 9	6 0

1) By principal *n*-side of a Cf. MARTINETTI and DE VRIES understand a group of *n* Cf-lines which contain together once all the Cf-points.

2) *Wiener Sitzungsberichte* 84, 1881.

3) *Göttinger Nachrichten*, 1889, N^o. 8.

1	1 1 1 8 2 3 2 3 4 5 1 2 3 5 7 1 2 4 3 6 1 2 3 4 5 a 2 4 6 9 4 7 6 5 6 7 8 0 4 6 9 9 5 7 0 8 0 7 6 9 8 b 3 5 7 0 8 8 9 9 0 0 a a a a b b b b b c c c c c c
2	1 1 1 8 2 3 2 3 4 5 1 2 3 4 5 1 2 3 4 5 1 2 3 6 7 a 2 4 6 9 4 7 6 5 6 7 8 7 0 9 6 9 0 6 7 8 0 5 4 8 9 b 3 5 7 0 8 8 9 9 0 0 a a a a b b b b b c c c c c c c
3	1 1 1 8 2 3 2 3 4 5 1 2 3 4 6 1 2 3 5 7 1 2 3 4 5 a 2 4 6 9 4 6 7 5 6 7 8 5 0 7 9 9 0 4 6 8 0 6 7 9 8 b 3 5 7 0 8 8 9 9 0 0 a a a a b b b b b c c c c c c c
4	1 1 1 8 2 3 2 3 4 5 1 2 3 4 5 1 2 3 4 5 1 2 3 4 7 a 2 4 6 9 4 6 7 5 6 7 8 0 7 9 6 9 6 0 7 8 0 5 4 9 8 b 3 5 7 0 8 8 9 9 0 0 a a a a b b b b b c c c c c c c
5	1 1 1 8 2 3 2 4 3 5 1 2 3 5 7 1 2 3 4 6 1 2 3 4 5 a 2 4 6 9 4 7 5 6 6 7 8 0 4 6 9 9 7 5 0 8 0 6 9 7 8 b 3 5 7 0 8 8 9 9 0 0 a a a a b b b b b c c c c c c c
6	1 1 1 8 2 3 2 4 3 5 1 2 3 4 5 1 2 3 4 6 1 2 3 5 7 a 2 4 6 9 4 7 5 6 6 7 8 7 9 0 6 9 0 5 7 8 0 6 4 8 9 b 3 5 7 0 8 8 9 9 0 0 a a a a b b b b b c c c c c c c
7	1 1 1 8 2 3 2 4 3 5 1 2 3 4 5 1 2 3 4 6 1 2 3 5 7 a 2 4 6 9 4 7 5 6 6 7 8 0 9 7 6 9 7 5 0 8 0 6 4 8 9 b 3 5 7 0 8 8 9 9 0 0 a a a a b b b b b c c c c c c c
8	1 1 1 8 2 3 2 5 3 4 1 2 3 4 5 1 2 3 6 7 1 2 3 4 5 a 2 4 6 9 4 7 6 7 5 6 8 0 9 7 6 9 5 4 8 0 0 7 6 9 8 b 3 5 7 0 8 8 9 9 0 0 a a q a a b b b b b c c c c c c c
9	1 1 1 2 4 6 5 3 7 2 1 2 3 4 5 1 2 3 4 5 1 2 3 6 7 a 2 4 6 8 8 9 7 5 3 4 8 7 6 9 0 9 0 8 7 6 0 5 4 8 9 b 3 5 7 9 0 0 8 9 0 6 a a a a b b b b b c c c c c c c
10	1 1 1 3 5 7 2 6 4 2 1 2 3 4 6 1 2 3 4 6 1 2 3 4 5 a 2 4 6 8 8 9 7 5 3 4 8 5 7 9 0 9 0 5 7 8 0 9 6 8 7 b 3 5 7 9 0 0 8 9 0 6 a a a a b b b b b c c c c c c c
11	1 1 1 3 5 7 2 6 4 2 1 2 3 4 6 1 2 3 4 5 1 2 3 4 6 a 2 4 6 8 8 9 7 5 3 4 8 5 7 9 0 9 0 6 8 7 0 9 5 7 8 b 3 5 7 9 0 0 8 9 0 6 a a a a b b b b b c c c c c c c
12	1 1 1 3 5 7 2 6 4 2 1 2 3 4 5 1 2 3 4 6 1 2 3 4 6 a 2 4 6 8 8 9 7 5 3 4 8 0 6 9 7 9 5 7 8 0 0 9 5 7 8 b 3 5 7 9 0 0 8 9 0 6 a a a a b b b b b c c c c c c c
13	1 1 1 3 5 7 2 6 4 2 1 2 3 4 6 1 2 3 4 5 2 3 4 1 6 a 2 4 6 8 8 9 7 5 3 4 8 9 5 7 0 9 0 6 8 7 5 7 9 0 8 b 3 5 7 9 0 0 8 9 0 6 a a a a b b b b b c c c c c c c
14	1 1 1 2 4 6 5 3 2 3 1 2 3 5 7 1 2 3 4 5 1 2 3 4 6 a 2 4 6 8 8 9 7 5 7 4 8 4 0 6 9 9 6 8 7 0 0 5 7 9 8 b 3 5 7 9 0 0 8 9 0 6 a a a a b b b b b c c c c c c c
15	1 1 1 2 4 6 5 3 2 3 1 2 3 4 5 1 2 3 4 6 1 2 3 5 7 a 2 4 6 8 8 9 7 5 7 4 8 6 7 9 0 9 5 0 7 8 0 4 8 6 9 b 3 5 7 9 0 0 8 9 0 6 a a a a b b b b b c c c c c c c
16	1 1 1 3 2 7 5 6 4 2 1 3 4 6 2 1 2 3 4 5 1 2 3 4 6 a 2 4 6 8 8 9 7 5 3 4 8 7 9 0 5 9 7 6 8 0 0 9 5 7 8 b 3 5 7 9 0 0 8 9 0 6 a a a a b b b b b c c c c c c c
17	1 1 1 3 2 7 5 6 4 2 1 2 3 4 5 1 2 3 4 6 1 2 3 4 6 a 2 4 6 8 8 9 7 5 3 4 8 7 6 9 0 9 5 7 8 0 0 9 5 7 8 b 3 5 7 9 0 0 8 9 0 6 a a a a b b b b b c c c c c c c
18	1 1 1 3 2 7 5 6 4 2 1 2 3 4 6 1 2 3 4 5 1 2 5 4 6 a 2 4 6 8 8 9 7 5 3 4 8 9 5 7 0 9 7 6 8 0 0 5 7 9 8 b 3 5 7 9 0 0 8 9 0 6 a a a a b b b b b c c c c c c c
19	1 1 1 3 2 7 5 6 4 2 1 2 3 4 5 1 2 3 4 6 1 2 3 4 6 a 2 4 6 8 8 9 7 5 3 4 8 9 6 7 0 9 5 7 8 0 0 7 5 9 8 b 3 5 7 9 0 0 8 9 0 6 a a a a b b b b b c c c c c c c
20	1 1 1 3 2 7 5 6 4 2 1 2 3 4 5 1 2 3 4 6 1 2 3 4 6 a 2 4 6 8 8 9 7 5 3 4 8 9 6 7 0 9 7 5 8 0 0 5 7 9 8 b 3 5 7 9 0 0 8 9 0 6 a a a a b b b b b c c c c c c c

according to their rest figures. If we use the list of SCHROETER, then the rest figures of the triplets of the system of NETTO are resp.:

N (01...a...) *cyc.* all VII, (0..6.8..) *cyc.* ¹⁾ all VIII.

Their possible decompositions into principal five-sides are:

I	none			
II	two, see 1 and 2		in the preceding table	
III	two, „ 3 „ 4		„ „ „	
IV	none			
V	three, „ 5, 6, 7		„ „ „	
VI	one, „ 8		„ „ „	
VII	one, „ 9		„ „ „	
VIII	four, „ 10, 11, 12, 13		„ „ „	
IX	two, „ 14 and 15		„ „ „	
X	five, „ 16, 17, 18, 19, 20		„ „ „	

According to 4 these decompositions now give rise to 20 triple systems, among which occur with certainty all possible systems; however, they can be identical mutually and to **K** or to **N**. We now remark that VI and VII can be completed in but one way; so as soon as these rests occur the system is identical to **8**, resp. **9**; from this follows already that **K** and **8**, and likewise **N** and **9** are of the same type (see table page 292).

Now rest figure VII appears for **11** according to the triplet 37a; VI on the contrary for:

1, 2, 3, 4, 5, 6, 7, 10, 12, 13, 14, 15, 16, 17, 18, 19, 20

resp. according to the triplets:

123, 123, 145, 167, 123, 123, 47a, 37a, 35c, 57b, 56a, 79c, 49a, 27a, 18a, 35c and 60b;

so **11** is identical to **9** and **K**, the remaining are identical to **8** and **N** and we have proved:

that except the two known forms no triple systems of thirteen elements exist.

At the same time is evident that to recognise a given system it is sufficient to find a few rest figures until one meets either VII (or VIII in greater number than six) or II, III, V, VI, IX or X.

The preceding has moreover given a method ²⁾ to determine the

¹⁾ The cyclic order is here: 0 1 2 3 4 5 6 7 8 9 a b c.

²⁾ Compare DE VRIES *Versl. en Meded. Kon. Akad. v. Wet.* VI, p. 13, where in a more restricted sense the same method is used to trace the (exclusively *regular*) principal poly-sides of the Clf. τ_n . Such a principal poly-side however determines a triple system and reversely. Indeed, the cyclic systems of 13 and 15 appear already in the work of DE VRIES (l. c. p. 16 and 17), however without being regarded as such.

number of triple systems for arbitrary n (if only $\equiv 1$ or 3 , mod. 6), i.e. to classify all diagonalless

$$\text{Cff. } \left\{ \frac{n-1}{2}, \left(\frac{n(n-1)}{2 \cdot 3} \right)_3 \right\},$$

namely :

1. by starting from all possible :

$$\text{Cff. } \left\{ (n-3) \frac{n-7}{2}, \left(\frac{(n-3)(n-7)}{6} \right)_3 \right\},$$

2. by enumerating the Cff. of its diagonals, those are :

$$\text{Cff. } \left\{ (n-3)_3, \left(\frac{3(n-3)}{2} \right)_1 \right\},$$

3. by investigating in how many ways each of these Cff. can break up according to its lines into three principal $\frac{n-3}{2}$ sides,

4. by every time assuming the lines of such a poly-side to be convergent to one point and these three points to be collinear,

5. by arranging the obtained systems in types.

Already for $n=15$, however, this method is checked by the absence of the classification of Cff. $(12_4, 16_3)$ necessary for 1, of which only some six forms have been enumerated¹⁾. Let us restrict ourselves to the best known and most regular form, of HESSE :

$$\begin{array}{c} A \quad \begin{array}{cccc} 1 & 2 & 3 & 4 \\ \hline 5 | & a & b & c & d \\ 6 | & b & c & d & a \\ 7 | & c & d & a & b \\ 8 | & d & a & b & c \end{array} \end{array}$$

in which each point of the quadruplet $abcd$ is collinear to the points of the two other quadruplets in the same row of column, then *three* types of triple systems of 15 elements appear :

$$\begin{array}{l} \text{I. Complement} \quad xab, xcd, x12, x34, x56, x78, \\ \quad \quad \quad \quad \quad yac, ybd, y13, y24, y57, y68, \\ \quad \quad \quad \quad \quad z ad, zbc, z14, z23, z58, z67, \\ \quad \quad \quad \quad \quad xyz. \end{array}$$

All rests are A , the system is identical to the cyclic one²⁾ :

$$(1.2 \dots 5 \dots) ; (1.3 \dots 9 \dots) ; (1 \dots 6 \dots 11 \dots).$$

$$\begin{array}{l} \text{II. Complement} \quad xab, xcd, x12, x34, x56, x78, \\ \quad \quad \quad \quad \quad yac, ybd, y13, y24, y58, y67, \\ \quad \quad \quad \quad \quad z ad, zbc, z14, z23, z57, z68, \\ \quad \quad \quad \quad \quad xyz. \end{array}$$

¹⁾ Comp. the author's dissertation; "Bijdragen tot de theorie der configuraties", Amsterdam 1907, § 36.

²⁾ L. HEFFTER, *Math. Annalen*, Vol. 49.

There are three rests A , namely of

xyz , $x56$ and $x78$;

there are four rests B , i. e. of the type of the Cf. (16₃, 12₁) of DE VRIES of the composition

B	1	2	3	4
5	a	b	c	d
6	b	c	d	a
7	c	d	a	b
8	d	a	b	c

These rests appear for xab , xcd , $x12$, $x34$.

The other rests are of other types.

III. Complement xab , xcd , $x12$, $x34$, $x58$, $x67$,
 yac , ybd , $y13$, $y24$, $y56$, $y78$,
 zad , zbc , $z14$, $z23$, $z57$, $z68$,
 xyz .

Only xyz has rest A , there are no rests B , all other rests are of other types.

Whether by completing other Cf. (16₃, 12₁) other systems than the three above-mentioned will appear, remains undecided; at any rate B will lead in at least *one* way to II as it appears among its rests.

Anatomy. — “*About the function of the ventral group of nuclei in the thalamus opticus of man.*” By Prof. C. WINKLER and Dr. D. M. VAN LONDEN.

The following remarkable case was offered to our observation in the neurological clinical department of the Binnengasthuis.

An unmarried woman, aged seventy-seven, not having suffered previously of any serious illness, and somewhat dull of hearing during the last years, got one single but severe fit of dizziness three weeks before her admittance.

On Jan. 8th 1908 she was found in her room unconscious, and transported thence to the Binnengasthuis, on arrival there she was slightly wandering in her mind. This state continued for three days, afterwards she made no complaints either of pain or of paraesthesia. Incontinence never occurred. There was found sclerosis of the arteries and dilatation of the heart. The urine contained $\frac{1}{4}$ ‰ of albumen and hyaline-cylindres. After three months death ensued caused by

pneumonia. Clinical examination of the different organs of sense in this woman gave the following results:

Smell and taste are normal.

Sight has diminished on account of a beginning senile cataract, and has on both sides been reduced to $\frac{6}{24}$. The fundus oculi is plainly visible and does not show any alterations. There is no restriction of the visual area worth mentioning.

Hearing is very bad during the first time after her admittance. She is almost completely deaf. The whispering voice is not heard on either sides. After three weeks this disturbance is restored so far, that on the left the whispering voice is distinguished to a distance of 3 M. This degree of dullness of hearing continued till her death.

On both sides the tympanic membrane has suffered slight sclerotic degenerations.

The *sensibility* of the body is in all respects normal to the left, *on the contrary to the right it has considerably decreased*, in the following manner:

the tactile sensibility is entirely lost in the right hand and foot, in the lower part of arm and leg it has suffered great disturbance, somewhat less in shoulder and hip, and still less in the right half of the trunk, whilst in the right half of the face hardly any disturbance is to be observed. *The difference between the head and the point of a pin* is badly distinguished on the right side, except in the face. The latter disturbance, like that of the tactile sensibility, has its boundaries towards the left in the mid-dorsal and mid-ventral lines of the trunk and is most marked in hand and foot.

The *pain-sensibility* of the skin has likewise diminished to the right. Piercing of the skin is not at all perceived in the extremities, only feebly in the trunk, but almost normally in the face.

On the contrary *pinching* or *squeezing* of the deeper situated portions produces a much sharper perception of pain to the right than to the left. Vehement repelling movements are occasioned by it.

The perceptions of *intense cold* and *intense heat* have suffered great decrease in the right extremities, to a less degree in the right half of the trunk, whilst the disturbance is feeblest in the face.

Passive movements communicated to the fingers, the hand, the toes or the foot of the right side, are not perceived at all, however swift and extensive these movements may be. Movements performed with the articulations of the right elbow or knee are perceived badly, for movements with the articulations of the right hip and shoulder the perception is nearly normal. The patient has lost all notion as to the manner in which her right hand and foot are *placed in space*,

as regards the position of knee and elbow her perception is likewise inaccurate but to a less degree. The position of the upper-arm and leg is ascertained with tolerable accuracy. There is complete *astereognosis* of the right hand. Not a single object put into this hand is recognized. The patient does not know whether she has got something in this hand or not. Oftenest she drops it.

All these disturbances of sensibility to the right remained stationary during the three months the woman was under observation.

On the contrary the motility of the right limbs had suffered only slightly. In the week after the lesion she complained of a certain feebleness of the right extremities.

A paralysis however has never been observed. The complaint was a passing one, and the only fact ascertained was that the right shoulder hung somewhat lower than the left one. Rapid as well as subile movements could be performed with the right extremities, e. g. to count money, or to bring the finger to the top of the nose, were done nearly as well by the right hand as by the left. *Here is only a slight right-sided cerebral ataxy, and there does not exist any vestige of athetosis, or choreic or other involuntary movements.* The dynamometer in the hand reached 50 w. on both sides.

The skin reflex-actions, as the abdominal, cremaster- and plantar-reflex-actions, are normal and on both sides equal. The deep reflex-actions, those of the tendo Achillis and of the knee are not increased, there is no clonus of foot or knee. Neither is there a distinct difference of tonus, nor any atrophy in the muscles of the two halves of the body. There have been no disturbances of speech or articulation. As the patient had never learned reading or writing, possible disturbances in reading or writing were not to be stated. Her condition remained unaltered until her death on the 24th of March 1908.

The brains, which were kindly put at our disposition from the laboratory of Prof. KUHN, were indurated in formaline for a few days. Thereupon frontal sections of 1 cm. were made through both hemispheres. The *only* degeneration that may be observed macroscopically is a focal destruction in the medial and caudal portions of the left thalamus opticus.

Consequently for the purpose of microscopical examination there was made a series of frontal sections through the left hemisphere, the most proximal sections of these passing through the caudal ends of the frontal convolutions, the temporal pole and the commissura anterior, whilst the most caudal section passes behind the caudal end of the fissura Sylvii, through the caudal border of the gyrus supra-marginalis, the praecuneus and the splenium corporis callosi.

The nucleus caudatus, the nucleus lenticularis, the capsula interna and the frontal end of the thalamus opticus have not suffered any alteration. Neither has the whole of the nucleus anterior. About halfway the sections through the thalamus, the frontal commencement of the focal softening is found, as a small irregular square in the nucleus lateralis (fig. 1). The hearth consist of leucocytes, lying close to one another, in its wall the capillary vessels are found distended and surcharged with blood-cells.

In the following sections the hearth is rapidly expanding (see fig. II). Irregularly shaped, it is situated within the ventral nuclei ¹⁾, destroys the largest part of the nucleus ventralis *b*, encompasses like this nucleus the "centre médian" of LÉVY, and enters into the ventral nucleus *a* until near the regio subthalamica. The "Gitterschicht", the lamina medullaris externa and the regio subthalamica are untouched by it; consequently both, the lateral medullary mass of the red nucleus and the strata of the lemniscus, remain free from damage.

In the same region is found a smaller focus, as yet apparently separate, (but in reality connected with the larger hearth) in the principal portion of the nucleus medialis.

A little more caudalward (see fig. III) the hearth attains its largest extension. It is now situated in the ventral nuclei *a*, *b* and *c*, that are almost completely destroyed, it sends a narrow branch into the nucleus medialis, and proceeds straitened wedge-like towards the regio sub-thalamica, where it approaches very closely the radiations of the lemniscus-fibres and intercepts these.

Still more caudalward (see fig. IV) the position of the hearth has become such, that the ventral nucleus *a* is left free, whilst the nuclei *b* and *c* and likewise the posterior nucleus are absorbed by it. The corpus geniculatum mediale forms here likewise part of the hearth (but the radiation from the brachium conjunctivum corporis quadrigemini postici into the nucleus gen. medialis is left uninjured). The hearth continues by a long and narrow branch along the ventral side in the pulvinar thalami optici (see fig. V), ending there.

The corpus geniculatum laterale is no where touched by the hearth. Neither is the so-called "Gitterschicht" of ARNOLD.

From this focus secondary degenerations start into different areas, these degenerations are distinguished partly by the presence of granular cells, partly by the absence of medullated fibres in lighter-coloured areas in preparations after the WEIGERT-PAL method.

In the thalamus, the frontal end of which does not show any degenerative alterations (see fig. I) the posterior part of the medial

¹⁾ VON MONAKOW'S nomenclature of the nuclei Thalami is followed.

principal nucleus has assuredly lost fibres, especially in the portion situated caudal of the hearth. Such is likewise the case with the "Gitterschicht", although it is no where touched directly by the hearth. In the neighbourhood of this latter a great number of the fibres passing the Gitterschicht in their course from the thalamus towards the retro-lenticular portion of the capsula interna, are degenerated. Those degenerated fibres gather into an area, lying close to the "Gitterschicht", an area, which in preparations made after WEIGERT-PAL'S method, contrasts with its surroundings by its being light coloured, against the black coloured retro-lenticular portion of capsula. (see fig. IVa)²).

Situated at first lateral of the "Gitterschicht" (see fig. IVa), this area may be pursued caudalward (fig. IVa, fig. Va₁a₂, fig. VIa₁a₂a₃) and frontalward (fig. IIIa₁a₂ and fig. IIa₂). In the caudal sections its ventral boundary is the medullary triangle surrounding the corpus geniculatum externum (*W* in fig. III), expanding thence both in the stratum sagittale externum and in the stratum sagittale internum (see fig. III and fig. IV). In frontal sections this field is situated in the capsula interna, medialward from the caudal ending of the putamen nuclei lenticularis (fig. IIa₂).

This degenerated area may be followed in three directions:

1st in the medullary rays of three temporal convolutions (see fig. I—VIIa₁) least in the gyrus temporalis I,

2nd in the splenium corporis callosi (see fig. VI and VIIa₃)

3rd in the medullary rays of the gyrus supramarginalis and still for a large part in the gyrus centralis posterior (see fig. I—VIIa₂). When examined in glycerine preparations the medulla of these gyri is thickly interspersed with granular cells.

Summing up the abovetold facts, we find some definite disturbances of perception in an old woman, after a lesion produced by a hearth of degeneration strictly localized within the left thalamus. These disturbances are:

1st Temporary deafness on both sides, leaving as its stationary result a certain degree of dullness of hearing on both sides.

2nd On the right side a chronic loss of sensibility in all qualities of sense of the skin and the deeper-situated parts, almost complete in the distal ends of the extremities, less marked in the trunk and in the roots of the extremities, unimportant in the face. All this is not accompanied by any choreic movements on that side, whilst there is found only a very slight ataxy to the right.

² In the drawings the areas are represented too light-coloured.

Without any doubt these disturbances are dependent on that hearth.

The loss of hearing is probably connected with the destruction of the corpus geniculatum mediale. This destruction, together with the secondary atrophy towards the temporal radiation (see a_1 in the figures), suffice to explain a certain loss of hearing, according to experiments made by different investigators after very different methods.

It is only to be noted as a remarkable fact that the patient was at first completely deaf on both sides, although the lesion was only at the left side. Remarkable too is the rapid way in which an important amelioration of this deafness set in.

The area of degeneration (a_1 in the figures) does not attain in the first place the medullary cone of the temporal convolution turned towards the fissura Sylvii, but is situated in preference in the two other temporal convolutions. This may be a reason, that she did hear and understood the spoken word.

It is formed by degenerated fibres, arriving thither both from the stratum sagittale externum and from the stratum sagittale internum, as becomes evident especially in the more frontal sections. In the sections made more caudalward, a degenerated fascicle going towards the splenium corporis callosi may also be pursued.

Perhaps these facts may add something to an eventual explanation of the incomplete deafness on both sides after focal disturbances on one side of the brain. But leaving this aside as less important, we desire only to call attention to the chief point of this interesting case.

The *ventral groups of nuclei* in the thalamus opticus, more especially their caudal portions — and these nuclei only, with the exclusion of all others — *are found softened in the cerebrum of a person, who during life had lost all sensibility in the distal ends of the crossed extremities without choreic movements, without intensive cortical ataxy on that side, whilst the sensibility remained nearly intact in the face, and had suffered some decrease at the proximal ends of extremities.*

Similar strictly defined hearths of degeneration are very rarely found in hemi-anaesthesia, but they contribute important data to the study of the intra-cerebral course of the tracts for the general sensibility.

These tracts are less known by far than the intracerebral course of the tracts for sight and hearing.

Since TÜRCK in 1850 by his experimental researches gave the first impulse to the study of the intra-cerebral sensibility tracts, there has appeared an enormous amount of literature on this subject, which has been recapitulated with sufficient accuracy in the dissertation of LONG¹⁾ (under guidance of DÉJÉRINE). The chief result of this mass

¹⁾ EDOUARD LONG. Les voies centrales de la sensibilité générale. (Étude Anatomoclinique). Thèse de Paris. 1899.

of labour was, that at present it has become nearly generally assumed that the thalamus opticus, amongst other functions, also contributes to provide for the sensibility of the crossed half of the body.

From the side of the school of DÉJÉRINE this opinion has been put forth with marked emphasis in the excellent book of ROUSSY¹⁾, who includes the disturbance of sensibility in the crossed half of the body in his "syndrome thalamique."

But not even in this work is treated a hearth localized so exclusively on the thalamus opticus²⁾. The strict localization noted in our case justifies the thesis:

The caudal portions of the ventral groups of nuclei in the thalamus opticus take a similar part in the central projection of the sensibility of the skin and of the deeper portions in the distal ends of the crossed extremities (less completely of the trunk and of the roots of the extremities, hardly at all of the face) as that taken by the corpus geniculatum mediale in the central projection of the impressions from the cochlea and by the corpus geniculatum laterale in the projection of the impressions from the retina.

A case, closely resembling the one given here, has been described by VON MONAKOW³⁾. Unfortunately he could not dispose of sufficient clinical data, especially as regards the question whether there had been hemianaesthesia during life. On the other hand he has described with the most careful accuracy the secondary atrophic degenerations, consequent to the loss of the posterior ventral nuclei, these degenerations being nearly the same as in the case related in the foregoing. It appears to us that in this latter case the gyrus centralis posterior receives a greater number of fibres from the atrophic area than in this well-known case of VON MONAKOW, offering nevertheless many striking points of resemblance with it.

It is moreover an important fact that the face remained almost wholly exempt from the loss of sensibility. Perhaps this is somehow connected with the fact that the median principal nucleus and the centre médian remained likewise almost wholly free from the degenerative hearth. For in animals the secondary tracts of the trigeminus have been traced principally to the centre médian (WALLENBERG⁴⁾)

¹⁾ GUSTAVE ROUSSY. La couche optique et le syndrome thalamique. Paris, Steinhil. 1907.

²⁾ ROUSSY l. c. Compare cas JOSSAUME p. 229.

³⁾ C. VON MONAKOW. Zur Anatomie und Physiologie des unteren Scheitelläppchens. Arch. f. Psych. 1899. XXXI S. 1—74. Fall D'auj. Also conf. L. EDINGER, Erkrankung des Thalamus opticus. Bd. XXI. Arch. f. Ps. 1899. S. 657.

⁴⁾ ADOLF WALLENBERG. Secundaire Bahnen aus dem frontalen sensiblen Trigemuskern des Kaninchens. Anat. Anz. XXVI. 1905. S. 145—155.

together with the ventral nucleus, others also believe the medial nucleus to be connected with the N. trigeminus (ARRIENS KAPPERS¹); besides animals with a powerfully developed trigeminus (e. g. the mole) possess a large medial nucleus. Consequently in regard to this case the possibility is not to be denied that the medial nucleus may stand in some closer relation to the sensibility of the face than the ventral does.

The above described case represents an almost unique experiment taken by Nature, and it demonstrates, *that isolated destruction of the ventral thalamus-nuclei may be accompanied by loss of all sensible perception in the distal ends of the crossed extremities.*

EXPLANATION OF THE FIGURES.

Fig. I—VII, frontal sections through the left hemisphere. Fig. I is a section frontal from the red nucleus, which hits the corp. subthalamicum; the frontal beginning of the hearth. Fig. II through the red nucleus, the retrolenticular portion of the capsula interna here begins. Fig. III through the largest expansion of the hearth, the c. quadr. anterior is sectioned. Fig. IV through the corpora geniculata and pulvinar thalami. Fig. V the caudal end of the hearth in the pulvinar thalami.

In all sections *a.* indicates the area of degeneration in the retro-lenticular portion of the capsula interna, situated lateral from the Gitterschicht, $a_1 a_1$ the radiation of the degenerative field towards the temporal radiation, $a_2 a_2$ the radiation towards the gyrus supramarginalis and towards the gyrus centralis posterior, $a_3 a_3$ the radiation towards the corpus callosum.

Fig. VI, the section through the splenium corp. callosi. The degenerative areas.

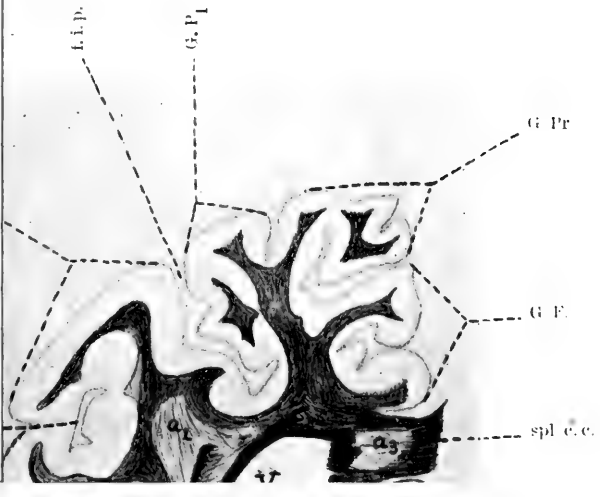
Fig. VII, through the splenium corp. callosi and the tapetum.

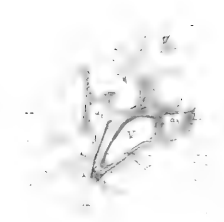
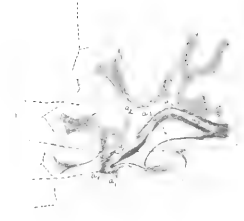
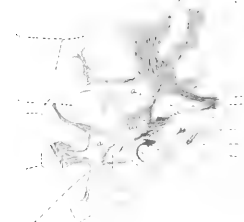
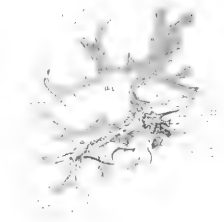
In all figures the signification of the letters employed is as follows:

cap. n. c. = caput nuclei caudati, caud. n. c. = cauda nuclei caudati, c. c. = corpus callosum, c. f. = columna fornicis, f. f. = fimbria fornicis, f. c. = fissura centralis, f. i. p. = fissura interparietalis, f. p. c. = fissura postcentralis; f. S. = fissura Sylvii, r. a. f. S. = ramus ascendens fissurae Sylvii, G. C. a. = gyrus centralis anterior, G. C. p. = Gyrus centralis posterior, G. s. M. = Gyrus supramarginalis, G. L. = gyrus lingualis, G. F. = gyrus fornicatus, G. H. = gyrus hippocampi, G. P₁ = gyrus parietalis superior, G. Para C. = gyrus paracentralis, G. Pr = gyrus praecunei, G. O. T. = gyrus occipito-temporalis, GT₁, GT₂, GT₃ = gyri temporales, l. m. e. = lamina medullaris externa thalami, l. m. i. = lamina medullaris interna, p. p. = pes pedunculi, pulv. = pulvinar thalami, n. ant. = nucleus anterior thalami, n. med. = nucleus medialis thalami, n. lat. = nucleus lateralis thalami, n. ventr. (a. b. c.) = nucleus ventralis thalami (a. b. c.), Gitt. = Gitterschicht, n. c. = nucleus caudatus, n. l. = nucleus lenticularis, N. R. = nucleus ruber, m. d. N. R. = medulla dorsalis nuclei rubri, s. n. = substantia nigra, c. L. = corpus subthalamicum, c. m. L. = centre médian (Luys), spl. c. c. = splenium corporis callosi, s. s. ext. = stratum sagittale externum, s. s. int. = stratum sagittale internum (radiation of GRATIOLET), str. t. = stria terminalis, tap. = tapetum, W. = stratum medullare corporis geniculati lateralis (WERNICKE'S triangular area), c. g. l. = corpus geniculatum laterale, c. g. i. = corpus geniculatum mediale.

¹) G. A. ARRIENS KAPPERS. Weitere Mitteilungen über die Phylogense des Corp. striatum und des Thalamus. Anat. Anz. 1908. Bd. XXXIII. No. 13 und 14, S. 321.

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Physics. — “*On the kinetic derivation of the second Law of Thermodynamics.*” By Dr. O. POSTMA. (Communicated by Prof. H. A. LORENTZ.)

§ 1. In a previous paper¹⁾ I tried to set forth how an ensemble of molecular systems possessing only kinetic energy may be thought gradually to pass to a state in which all the combinations of place and also all the combinations of velocity of the molecules occur with the same frequency. In this final condition the molecules of by far the majority of the systems of the ensemble will, as was shown, be distributed about uniformly over the vessel and have MAXWELL'S distribution of velocities.

This result, however, requires some amplification.

As the problem of the distribution of place and that of the distribution of velocity were treated quite separately, the above-mentioned result implies only, that in the end the molecules will be distributed uniformly over the vessel *for all the velocities together*, and that they will have MAXWELL'S distribution of velocities *for the vessel considered as a whole*. This, however, is not what is generally understood by uniform distribution over the vessel and MAXWELL'S distribution of velocities; we mean by this that even for a limited amount of velocities the molecules will be spread about uniformly over the vessel, and that even for a limited portion of the vessel MAXWELL'S distribution of velocities will hold on the main. So the question remains, how this result may be obtained.

Let us first observe that in a canonical or microcanonical ensemble the uniform distribution of place and MAXWELL'S distribution of velocities in the latter sense is really obtained. This is very easily seen for the canonical ensemble. It is, however, also the case for a microcanonical ensemble, where the frequency of a certain distribution of place and velocity is proportional to the number of combinations possible. This number of combinations may be given

in the form $Ce^{-\iint f \log f \, d\omega \, d\omega}$ just as it is given in the form

$Ce^{-\int f \log f \, d\omega}$ when only the distribution of the velocities is considered.

So in the most frequently occurring system — $\iint f \log f \, d\omega \, d\omega$ or — H is maximum. With given kinetic energy this is the case, if

¹⁾ These Proc. X, p. 390.

$f = ae^{-b(\frac{x^2}{2} + \frac{y^2}{2} + \frac{z^2}{2})}$, where a and b are real constants, so that for this system MAXWELL'S distribution of velocities holds for any small part of the vessel, and also the density is constant throughout the vessel for one definite velocity. That for the great majority of the systems the distribution of place and velocity differs little from the maximum occurring one may be shown in the same way as it is shown when the distribution of place and velocity is considered separately.

It is, however, easy to see that if an ensemble arises, not a microcanonical one, indeed, but one, for which the mean density becomes constant for finite but small extension elements, by approximation the same result will be obtained as we have for a microcanonical ensemble, viz. uniform distribution throughout the vessel and MAXWELL'S distribution of velocities, and that with greater accuracy as the elements are smaller. So we shall have a kinetic derivation of the 2nd law of thermodynamics, if we can show that an arbitrary ensemble of systems with a definite kinetic energy passes into such a "rough" microcanonical ensemble. So this has again led us to the quantity called "entropie grossière" by POINCARÉ, for if Π , the mean density over the elements δ , becomes constant, $\sum \Pi \log \Pi \delta$ or the entropie grossière decreases. It seems to me that we might demonstrate in the following way that Π becomes constant in course of time.

Let us in the first place once more consider the ensemble of planets or one-dimensional moving molecules discussed in § 2 and § 3 of the above-mentioned paper. It was shown that this ensemble moves in such a way that finally all places occur equally frequently. This was the case for all the velocities together and happened just because all kinds of velocities occurred for the systems. If, however, the total amount, over which the velocities of the systems (planets or molecules) extend, is divided into small, but finite portions, it will also hold for these amounts separately, if we only take the time long enough. So when these amounts extend from ω_1 to $\omega_1 + \Delta\omega$, from $\omega_1 + \Delta\omega$ to $\omega_1 + 2\Delta\omega$ etc. the systems with velocities lying between ω_1 and $\omega_1 + \Delta\omega$ will finally be uniformly distributed over all the values l lying between 0 and 2π ; in the same way the systems with velocities between $\omega_1 + \Delta\omega$ and $\omega_1 + 2\Delta\omega$ etc. Each of the horizontal strips of fig. 1 lying above each other contains then the same number of representing points.

If instead of an ensemble of single planets or single molecules we take an ensemble of systems of n molecules each but disregard the collisions, the same reasoning will hold. The whole of the representing points now moves, however, in a $6n$ -dimensional space, and instead of the axis of distances and the axis of velocities we get now the space

of coordinates and the space of velocities. Also if we do not neglect the collisions a motion of the ensemble will take place in the moments

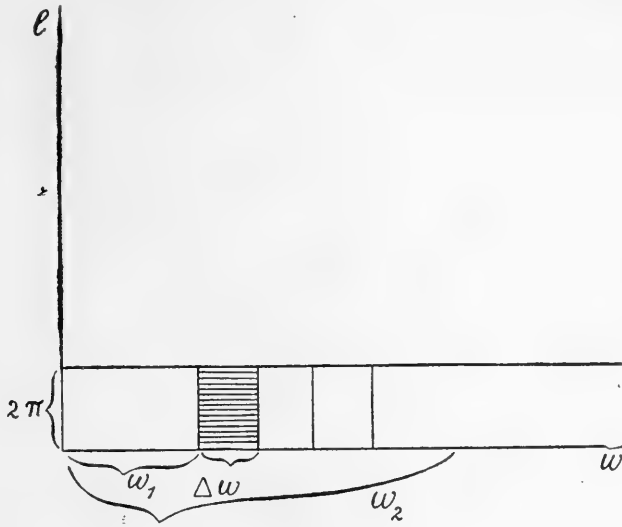


Fig. 1.

between the collisions in the indicated direction, so to the state with uniform mean density in the narrow strips extending lengthwise over a small but finite distance, bounded by the same combinations of velocities (symbolically represented by the horizontal regions *a* of fig. 2). In consequence of the collisions, however, the mean density in narrow vertical regions approaches uniformity. Nor need these

comb. of place

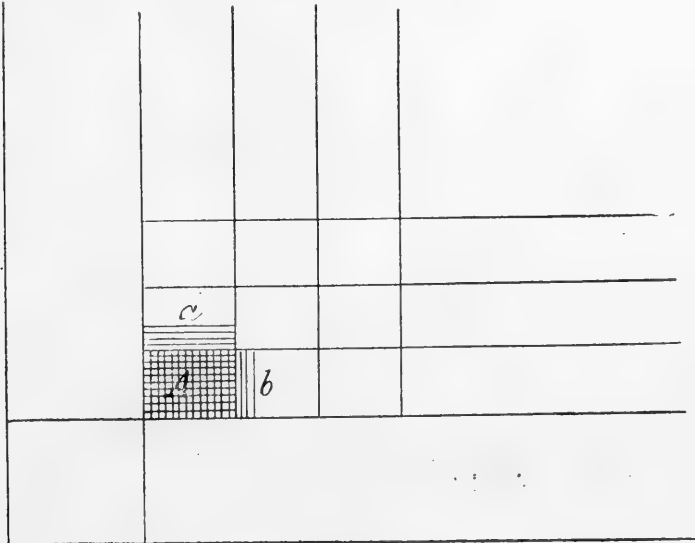


Fig. 2.

comb. of velocities

regions extend over the total amount of possible combinations of place, but the approach to uniformity is also found over finite small portions of this amount, (the regions b). What happens now if the two actions take place simultaneously? In the collision the representing points shift in horizontal direction, which modifies the distribution in the regions a , and the first action, which would make the distribution over the regions a uniform, is counteracted. This continues to be the case, as we think the regions a infinitely narrow; if however, we consider an element from the figure, the horizontal dimension of which is indicated by a , and the vertical dimension by b (the rectangle A), then the distribution in the elements A lying one above the other will also approach to uniformity by the first action whereas the disturbing influence with which the second action counteracts the first, will continually decrease and approach to zero. So it seems to me that we may assume that the mean density in the elements A lying above each other becomes the same in course of time; this reasoning will, however, also hold for the elements lying side by side in horizontal direction (if we take now the second action as the principal one, and the first as the disturbing action), so that we get a "rough" microcanonical ensemble in the end¹⁾.

If the above reasoning is correct, we have obtained the result that every arbitrary ensemble of molecule systems with purely kinetic energy proceeds towards a state where uniform distribution of place and MAXWELL'S distribution of velocities is most frequent. In the meantime we must assume that every system in itself has a reversible motion and so after some time it will get again very near to its initial state, and will do so repeatedly. Whether BOLTZMANN'S $H = \iint f \log f \, do \, d\omega$ will decrease for the majority of the cases depends on the initial state of the ensemble. It is conceivable that this state is such that the majority of the systems are nearer to the state occurring finally maximum than is the case for a micro-canonical ensemble; then the H would increase instead of decrease for those systems. It is, however, evident, that this will not be the case for an ensemble that represents a system in which recently some disturbance of equilibrium has taken place. For such a system H will most probably decrease.

¹⁾ It would be doing GIBBS an injustice if we did not admit, that in his Statistical Mechanics he already pointed to this remaining constant of the entropic fine, in opposition to the decrease of the entropic grossière when he says treating the analogy of the coloured liquid: "If treating the elements of volume as constant . . . etc." p. 145.

§ 2. Now the question may be raised what place we have to assign to BOLTZMANN'S proof that $H = \iint f \log f \, d\omega \, d\omega_1$ would decrease for an "ungeordnetes" system with regard to the above reasoning and the one preceding it. H seems to have to decrease for such a system, which as ZERMELO and others pointed out can hardly be always the case for one definite system, and can only be assumed as occurring in general for an ensemble.

In the first place we must observe with regard to this that by no means certainty prevails that a system which is in an "ungeordnet" state at a certain moment, will continue to be in such a state.

In the second place the properties of such a system, as BOLTZMANN applies them in the derivation of the variation of the function H in consequence of the collisions (see form. 17 and 105), can occur for one definite system with a sufficient degree of accuracy only when the elements $d\omega$, $d\lambda$ etc. occurring in these formulae, are taken rather large. There are, however, also objections to this (as that it is assumed that in a collision of two molecules the velocity-points always get outside the elements $d\omega$ and $d\omega_1$).

Independent of the size of the elements the property of being "ungeordnet" cannot occur for one definite system, it can, however, for the average of a whole ensemble (or in course of time if we think the systems taken at random from a certain ensemble).

This ensemble is formed by the whole of the possible systems obtained if we think the places and velocities of the n molecules assigned to them by chance, so that every time the chance to a certain combination of place and velocity is represented by a constant function f of the coordinates and velocities. If n is large, the majority of these systems have a distribution of place and velocity the course of which is mainly indicated by the function f . It does not hold exactly for any definite system that in the neighbourhood of every molecule the number of molecules of a certain kind are determined by the size of the spacial element considered and the f holding there, but on an average it does hold for the whole ensemble. So we may say that this ensemble represents BOLTZMANN'S "ungeordnetes" system. On an average $\frac{dH}{dt}$ would, therefore, be negative for this ensemble.

On further comparison of BOLTZMANN'S way of treatment and the results of § 1 we meet with an important point of difference. On the whole H will decrease for the majority of the systems for an arbitrary ensemble on account of the tendency towards uniformity

of density over the elements of extension indicated by A in fig. 2. This tendency proceeded from two actions, the former giving uniform density over the horizontal, the latter over the vertical regions. So we might say that the decrease of H is brought about both by the motion of the molecules (the first action) and by the collisions (the second action). The coordinates and the velocities occur also in H in the same way.

Yet BOLTZMANN states expressly that the H can only decrease in consequence of the collisions¹⁾ and he shows this as follows:

The change of H within a given surface is determined by

$$\frac{d}{dt} \sum_{v,0} \log f = \iint d\omega \, d\omega \left[\frac{\partial f}{\partial t} - \log f \left(\xi \frac{\partial f}{\partial x} + \eta \frac{\partial f}{\partial y} + \zeta \frac{\partial f}{\partial z} + X \frac{\partial f}{\partial \xi} + Y \frac{\partial f}{\partial \eta} + Z \frac{\partial f}{\partial \zeta} \right) \right] + C_4 (\log f) + C_5 (\log f).$$

If the surface is made to join the walls of the vessel, the first term is zero, the terms with X , Y , and Z are lost if we assume that there are no external forces; C_4 and C_5 denote the change caused by the collisions. The change in consequence of the motion of the molecules is equal to:

$$- \iint d\omega \, d\omega \log f \left(\xi \frac{\partial f}{\partial x} + \eta \frac{\partial f}{\partial y} + \zeta \frac{\partial f}{\partial z} \right).$$

BOLTZMANN shows that this integral is equal to:

$$\iint d\omega \, dS \, fN - \iint d\omega \, dS \, Nf \log f$$

which is to be integrated over the surface S , which includes the considered gas mass. From this follows that the increase in H in consequence of the motion is equal to the quantity that is brought into the surface S by the molecules. So if the gas is left to itself, this quantity will be zero, so that H does not change in consequence of the motion, but only in consequence of the collisions²⁾. No doubt we shall have to look for the explanation of this difference in result to the fact that BOLTZMANN considers the "entropic fine", whereas above the "entropic grossière" was considered. If the elements $d\omega$ and $d\omega$ are taken of finite size, as must be done here, the calculations which reduce the change in H to a surface integral, must not be adopted in unmodified form.

§ 3. For a kinetic derivation of the 2nd law of thermodynamics it is necessary kinetically to define a quantity which agrees in

¹⁾ See: Vol. I, p. 126, note.

²⁾ Cf. LORENTZ, "Abhandlungen über Theoretische Physik", Abhandl. VIII.

properties with the thermodynamic entropy. These properties are :

1. For reversible changes from one state of equilibrium into the other is $\frac{dQ}{T}$ the differential of a quantity which is defined as entropy ;
2. in an isolated system which, as a whole, is not in equilibrium, but may be divided into parts which are, the total entropy increases. We saw above that in general the quantity introduced by BOLTZMANN

$$H = \iint f \log f \, do \, d\omega$$

decreases, also when the system does not consist of parts, each in itself in equilibrium. So if we consider a quantity proportional to $-H$ as entropy, it will certainly satisfy the second condition in by far the majority of cases. As to the first condition, this is satisfied as LORENTZ has shown²⁾, if $-\frac{2}{3}\mu$ is taken for the constant by which H is multiplied, in which $\mu = \frac{\text{mean kin. energy per mol.}}{\text{abs. temperature}}$. For a gas in stationary state

$$f = C e^{-\frac{3m}{4k}(\xi^2 + \eta^2 + \zeta^2)} = n \sqrt{\left(\frac{3m}{4\pi k}\right)^3} e^{-\frac{3m}{4k}(\xi^2 + \eta^2 + \zeta^2)}$$

so that

$$\begin{aligned} -\frac{2}{3}\mu H &= -\frac{2}{3}\mu N \left(\log C - \frac{3}{2} \right) = \\ &= \frac{2}{3}\mu N \log v + \mu N \log \mathfrak{D} - \frac{2}{3}\mu N \log N - \mu N \log \frac{3m}{4\pi\mu} + \mu N \end{aligned}$$

for which LORENTZ writes :

$$\frac{2}{3}\mu N \log v + \mu N \log \mathfrak{D} + C'.$$

At a given temperature we may, accordingly, write $N \left(\log \frac{N}{v} + C \right)$ also for H , in which C still contains \mathfrak{D} , no longer N and v .

Besides this entropy of Boltzmann different quantities have been kinetically defined by GIBBS, which, according to him, possess the properties of the entropy. The most prominent of them is the $-\eta$ or $-\int P \log P \, d\mathbf{r}$, being the negative mean \log of the density over the canonical ensemble which represents the system in equilibrium. As

²⁾ Cf. l.c. Abhandlung VIII.

was shown by LORENTZ¹⁾ this quantity has the property that in reversible changes of the system the differential is equal to $\frac{dQ}{T}$, in which T , the modulus of the ensemble, has the properties of the temperature. This entropy was only defined by GIBBS for the state of equilibrium. When, however, we represent a gas which is not in equilibrium by a non-canonical ensemble, and define the entropy in the same way, also the second property will hold for this entropy; the quantity $\int P \log P d\tau$ will namely gradually decrease if the elements $d\tau$ are not taken *infinitely* small, because each portion of the ensemble with given energy approaches to a rough micro-canonical one. In the special case considered in thermodynamics that the parts of the system are in equilibrium this will also be the case²⁾.

Calculating this $-\eta$ for a perfect gas, we find, as

$$-\eta = \frac{\bar{\epsilon} - \psi}{T}$$

whereas

$$\bar{\epsilon} = \frac{3}{2} NT \text{ and } -\frac{\psi}{T} = \frac{3}{2} N \log (2\pi mT) + N \log v,$$

$$-\eta = \frac{3}{2} N + \frac{3}{2} N \log (2\pi mT) + N \log v.$$

When comparing this value with BOLTZMANN's entropy we must bear in mind that this T does not agree perfectly with the \mathfrak{D} of BOLTZMANN; viz.:

$$\mathfrak{D} = \frac{\text{mean kin. energy per mol.}}{\mu} \text{ and } T = \frac{\text{mean kin. energy per system}}{\frac{3}{2} N}.$$

From this follows $T = \frac{2}{3} \mu \times \text{mean } \mathfrak{D}$ (taken over the ensemble).

So for comparison we must take:

¹⁾ See Abhandlung XI.

²⁾ The objection advanced by LORENTZ to this way of defining the entropy, that it would namely be difficult to understand how a non-canonical ensemble should be determined by a system that is not in equilibrium, does not seem to be conclusive to me. It is true, that the entropy and the ensemble are not determined in the same way as for a stationary system, but as we know more about the place and the velocities of the molecules or the way in which they have assumed their places and velocities, the ensemble is determined more accurately. If we e.g. know that everywhere a certain pressure and temperature prevails, we consider the ensemble as a sum of canonical ensembles, etc.

$$-\frac{2}{3}\mu\bar{\eta} = \mu N + \mu N \log \left(\frac{4}{3} \pi \mu m \vartheta \right) + \frac{2}{3} \mu N \log v,$$

for which we may also write:

$$\frac{2}{3} \mu N \log v + \mu N \log \vartheta + C'';$$

this C'' , however, does not agree with LORENTZ' C' .

In this connection I will finally call attention to an objection to the use of this latter entropy introduced by GIBBS.

Purely thermodynamically the entropy is determined by the diff.

equation $\frac{dQ}{T} = d\eta$. So this η contains an arbitrary additive constant.

This is not the case for the kinetically defined one. BOLZMANN'S H

is entirely determined by the equation $H = \int \int f \log f \cdot d\omega$ and so

also the entropy $-\frac{2}{3}\mu H$. In the same way in GIBBS $-\bar{\eta} = -\int P \log P d\tau$,

if the energy is purely kinetic, which we shall assume.

The same applies to the free energy ψ , thermodynamically it contains an arbitrary additive constant, kinetically it does not. This uncertainty, however, allows us to choose the constant in thermodynamics in a convenient way, which is no more possible in the kinetic theories. This constant is now chosen in such a way that the ψ for a certain gas mass (and then also the η) is equal to the sum of the ψ 's of the parts (molarly not molecularly separated). This appears clearly in LORENTZ¹⁾. Here a gramme molecule of a certain gas is considered, and

$$\psi = -RT \log v + C \text{ derived from } \frac{\partial \psi}{\partial v} = -p = -\frac{RT}{v}.$$

Now C is chosen in such a way, that $\psi = 0$ if $v = 1$, so $C = 0$ or $\psi = -RT \log v$. Somewhat further it says: "Haben wir es nicht mit einer, sondern mit m Einheiten zu tun, die zusammen das Volum v füllen, so haben wir nebeneinander m -mal die Einheit in dem Volum $\frac{m}{v}$. Wir müssen also in $\psi = -RT \log v$ durch $\frac{m}{v}$ ersetzen und dann mit m multiplizieren." So by definition the ψ of the whole has here evidently been put equal to the sum of the ψ 's of the parts occurring side by side in the volume v .

We may also say that this has taken place by assigning another value to C for every quantity. If namely in a volume $2v$ we had

¹⁾ l. c. p. 236.

two unities side by side, we should have for the first $\psi_1 = -RT \log v$, for the second $\psi_2 = -RT \log v$, so $\psi_1 + \psi_2 = -2RT \log v$. For the total quantity we should have $\psi = -2RT \log 2v + C$; if now we had again put $C = 0$ (so that $\psi = 0$ if $2v = 1$) then ψ would not have been $= \psi_1 + \psi_2$. The C , however, has now been chosen in such a way that $\psi = 0$ if $2v = 2$ or $C = 2RT \log 2$ and hence $\psi = -2RT \log v = \psi_1 + \psi_2$.

In connection with this we have the property that if two quantities of different gases, being in equal volumes at the same T , are mixed in the same volume at the same T , the free energy remains the same, whereas it decreases if this is done with two quantities of the same gas. A similar property exists for the entropy (GIBBS'S paradox). How is this now for the kinetically defined entropy or free energy? To answer this question we shall successively discuss: 1. is the entropy of an homogeneous gas mass in a volume $2v$ double that of half the quantity in a volume v ; 2. is the entropy of an homogeneous gas mass in a volume v greater than the sum of the entropies of two such masses forming together the first quantity each in an equal volume v ; 3. is the entropy of a mixture of 2 gases equal to the sum of the entropies of the two gases separately? In the entropy of BOLTZMANN the answer is every time affirmative.

If we consider $H = N \left(\log \frac{N}{v} + C \right)$, then in the 1st case $H_1 = N_1 \left(\log \frac{N_1}{v} + C \right)$, so $2H_1 = 2N_1 \left(\log \frac{N_1}{v} + C \right)$; further for the whole mass in the volume $2v$:

$$H = 2N_1 \left(\log \frac{2N_1}{2v} + C \right) = 2N_1 \left(\log \frac{N_1}{v} + C \right) = 2H_1.$$

In the second case:

$$H_1 = N_1 \left(\log \frac{N_1}{v} + C \right), \quad H_2 = N_2 \left(\log \frac{N_2}{v} + C \right),$$

so $H_1 + H_2 = N_1 \log N_1 + N_2 \log N_2 - (N_1 + N_2) (\log v + C)$, while $H = (N_1 + N_2) \log (N_1 + N_2) - (N_1 + N_2) (\log v + C)$, so that $H < H_1 + H_2$, or the entropy of the whole is greater than the sum of the entropies of the parts.

In the 3rd case the formula for H used here does not hold, but now BOLTZMANN puts here $H = H_1 + H_2$ by definition. For a mixture of two gases BOLTZMANN puts viz.:

$$H = \iint f \log f \, d\omega + \iint f_1 \log f_1 \, d\omega.$$

However, also the questions 1 and 2 might have been answered

directly from this definition. $H = \iint f \log f \, d\omega$ indicates, namely, that H of the whole = ΣH of the parts; further we can always think the molecules divided into two parts with densities f_1 and f_2 , so that $f = f_1 + f_2$,

$$(f_1 + f_2) \log (f_1 + f_2) < f_1 \log f_1 + f_2 \log f_2,$$

so that also $H < H_1 + H_2$. From this latter way of treatment appears at the same time that the three properties are also valid for the entropy of BOLTZMANN if the gas is *not* in the state of equilibrium.

To answer the same questions with regard to the entropy of GIBBS we consider the formula:

$$-\eta = \frac{3}{2} N + \frac{3}{2} N \log (2\pi mT) + N \log v.$$

As to the first question for N_1 molecules in the volume v :

$$-\bar{\eta}_1 = \frac{3}{2} N_1 + \frac{3}{2} N_1 \log (2\pi mT) + N_1 \log v,$$

so

$$-2\bar{\eta}_1 = 3N_1 + 3N_1 \log (2\pi mT) + 2N_1 \log v$$

and for $2N_1$ mol. in volume $2v$:

$$-\bar{\eta} = 3N_1 + 3N_1 \log (2\pi mT) + 2N_1 \log 2v,$$

so that the entropy of the whole is *not* equal to the sum of the entropies of the parts. The *increase* in entropy (or free energy) of the whole, however, is always equal to the increase in entropy (or free energy) of the parts¹⁾.

As far as the second and third questions are concerned, we may directly take the general case of a mixture of two different gases and find then:

$$e^{-\frac{\psi}{T}} = (2\pi T)^{\frac{3N}{2}} \frac{1}{m_1^{\frac{3N_1}{2}}} \frac{1}{m_2^{\frac{3N_2}{2}}} \frac{1}{v^N}$$

from which:

$$-\frac{\psi}{T} = \frac{3N}{2} \log (2\pi T) + \frac{3N_1}{2} \log m_1 + \frac{3N_2}{2} \log m_2 + N \log v$$

¹⁾ Accordingly the equation derived by Dr. L. S. ORNSTEIN in his Thesis for the Doctorate: "Application of GIBBS's Statistical Mechanics to molecular-theoretical problems", (Leiden 1908) p. 54:

$\sum_1^k (\psi_x - \psi_{0x}) = \psi - \psi_0$ states only that the *increase* in ψ of the joint elements forms the total increase in ψ of the whole. For the "zero-state", for which ψ_{0x} and ψ_0 hold, viz. the state in which the potential energy = 0, $\sum \psi_{0x} = \psi_0$ is by no means valid. It is exactly this "zero-state", that has been considered above.

and

$$-\bar{\eta} = \frac{3N}{2} + \frac{3N}{2} \log(2\pi T) + \frac{3N_1}{2} \log m_1 + \frac{3N_2}{3} \log m_2 + N \log v.$$

For the first substance alone we find:

$$-\bar{\eta}_1 = \frac{3N_1}{2} + \frac{3N_1}{2} \log(2\pi T) + \frac{3N_1}{2} \log m_1 + N_1 \log v,$$

for the second alone:

$$-\bar{\eta}_2 = \frac{3N_2}{2} + \frac{3N_2}{2} \log(2\pi T) + \frac{3N_2}{2} \log m_2 + N_2 \log v.$$

From this appears $-\bar{\eta} = -\eta_1 + -\eta_2$ or the entropy of the mixture is equal to the sum of the entropies of the gases forming the mixture, which now holds too if the component parts consist of the same gas. So there is no perfect harmony with thermodynamics: for this entropy GIBBS's paradox no longer holds.

That the $-\bar{\eta}$ of the whole volume is not equal to the $\Sigma -\bar{\eta}$ of the parts is a consequence of the fact that the extension in phase $v_1^{N_1} \times v_2^{N_2}$ is not equal to the extension $(v_1 + v_2)^{N_1 + N_2}$. In the total volume there are more possibilities of combination of place than when the volume has been divided into two separate parts. We may also say that BOLTZMANN's entropy just as in thermodynamics, may be divided with regard to the volume, GIBBS's entropy with regard to the molecules. If we compare the formulae :

$$H = N \left(\log \frac{N}{v} + C \right) \text{ and } \bar{\eta} = N (-\log v + C),$$

it appears that GIBBS's entropy can be brought into harmony with thermodynamics by augmenting $\bar{\eta}$ by $N \log N$ or $N (\log N + C)$. This may be done by multiplying the density $e^{\bar{\eta}}$ by N^N , e^{-N} or $N!$ by approximation. So we should have to take for $\bar{\eta}$ the mean \log of the density, not with respect to the *specific*, but with respect to the *generic* phases. ¹⁾

1) When I had written the above, I observed that the last remarks are not new. In the last sentence of his book GIBBS himself has already made the observation that we shall have to take $-\bar{\eta}_{gen}$ and not $-\bar{\eta}_{spec}$ as equivalent for the entropy, "except in the thermodynamics of bodies in which the number of molecules of the various kinds is constant." So it will always have to be done where the entropy of the whole is compared with that of the parts.

Nevertheless considering that GIBBS devotes so few words to the matter, I feel justified in not suppressing my remarks.

Physics. — “On the law of molecular attraction for electrical double points.” By Prof. J. D. VAN DER WAALS JR. (Communicated by Prof. J. D. VAN DER WAALS).

Though Prof. M. REINGANUM has sometimes expressed the opinion that from the supposition that the molecules are electrical double points would follow that the molecular attraction decreases proportionally to $\frac{1}{r^4}$, he pointed out to me in a private letter that his deduction of the equation of state does not depend upon the accuracy of this opinion. In fact for every pair of molecules we have for the value of the potential energy

$$-\frac{m}{3r^3} \sqrt{3 \cos^2 \vartheta + 1} \cdot \cos \varphi$$

and so for the virial i. e. for $\frac{1}{2} rR$ — if r represents the line joining the molecules and R the component of the molecular force in the direction of this line —

$$\frac{m}{2r^4} \sqrt{3 \cos^2 \vartheta + 1} \cdot \cos \varphi,$$

so the ratio $\frac{\text{virial}}{\text{potential energy}} = \frac{3}{2}$.

As this ratio has the same value for each pair of molecules, it is also the ratio between the total virial of the attracting forces of all the molecules and the total potential energy. And it is this ratio which REINGANUM uses for his deduction of the equation of state.

So we see that this ratio has the same value as if the attraction decreased proportionally to $1/r^4$, though in reality the mean attraction decreases much more rapidly. If we wished to calculate this ratio by differentiating the value for the mean potential energy¹⁾ with respect to r , in order to find the force, and by multiplying this value by $\frac{1}{2} r$ in order to find the virial, we should find a value different from $\frac{3}{2}$. This is because we should not differentiate the *average* potential energy in order to find the *average* force, as I have i.e. erroneously written. In order to find the average force we must first find the force between two molecules by differentiating the potential energy with respect to r . Then we must multiply the result by :

$$\frac{m^2 \sqrt{3 \cos^2 \vartheta + 1} \cdot \cos \varphi}{3r^3} \frac{1}{4} \sin \varphi \, d\varphi \sin \vartheta \, d\vartheta.$$

¹⁾ These proceedings XI, p. 132.

and integrate with respect to φ and ϑ . It is not allowed to change the order of these operations: to integrate first and to differentiate afterwards, as we should do if we calculated the attraction by differentiating E with respect to r . This is obvious from mathematical considerations, but it can also easily be shown from physical considerations. For we saw that the double points have yielded in a higher degree to the couples they exercise on one another, according as they have approached one another more closely.

If therefore we make a group of bipoles approach another bipole from a distance r_2 to a distance r_1 , and if we want the axes of the bipoles, when they are at the distance r_1 to be orientated in the same way as may be expected from the laws of probability, then we must make the bipoles turn in the direction of the couples at the same time as they approach to the fixed double point. The loss of potential energy is therefore not equal to the work of the attracting forces but contains also the work of the couples and therefore we cannot find the average force by differentiating the average potential energy with respect to r .

The attraction of each pair of molecules is found by differentiating $-\frac{1}{3r^3} \sqrt{3 \cos^2 \vartheta + 1} \cdot \cos \varphi$ with respect to r , i.e. by multiplying this quantity by $-\frac{3}{r}$. Therefore we find also the value of the average force by multiplying the value of the average potential energy by $-\frac{3}{r}$; so we find:

$$K = t \sqrt{3} \left\{ \frac{m^4}{9t^2 r^7} \frac{p_1}{3!} + \frac{2m^2 p_2}{3^2 t^2 r^6} \frac{p_2}{5!} + \frac{3m^4 p_3}{3^4 t^4 r^{12}} \frac{p_3}{7!} + \dots \right\}$$

where the quantities p have the same signification as on p. 136 l.c.

It appears that the way in which the attraction depends on r is the same as I had indicated l.c., but that the coefficients have another value than we should find by differentiating E with respect to r .

Physics. — “*Contribution to the theory of binary mixtures*”. X. By Prof. J. D. VAN DER WAALS.

THE INTERSECTION OF THE CURVES $\frac{d^2\psi}{dx^2} = 0$ AND $\frac{d^2\psi}{dv^2} = 0$.

The points in which the two curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2}$ intersect, lie of course in the unstable region. For it is required for the points of the spinodal line, the limit of the unstable region, that $\frac{d^2\psi}{dx^2} > 0$ and $\frac{d^2\psi}{dv^2} > 0$, and the product $\frac{d^2\psi}{dx^2} \frac{d^2\psi}{dv^2} = \left(\frac{d^2\psi}{dx dv}\right)^2$. Hence the use of the study of the way in which these two curves intersect, must not be looked for exclusively, nor even chiefly, in an indication for the course of the spinodal curve. It is, indeed, clear and has been repeatedly set forth in the previous papers that only in the cases in which there is intersection between the two curves, or when $\frac{d^2\psi}{dx^2} = 0$ lies outside the curve $\frac{d^2\psi}{dv^2} = 0$, the spinodal line deviates greatly from $\frac{d^2\psi}{dv^2} = 0$; whereas, when $\frac{d^2\psi}{dx^2} = 0$ lies entirely within $\frac{d^2\psi}{dv^2} = 0$, the course of the spinodal line deviates little from the course of $\frac{d^2\psi}{dv^2} = 0$. But above all the knowledge of the relative position of $\frac{d^2\psi}{dx^2} = 0$ compared with $\frac{d^2\psi}{dv^2} = 0$ seems of importance to me for the question whether for a given binary mixture three-phase-pressure is to be expected or not. And everything that can contribute to elucidate a matter of such practical importance, must necessarily be considered important. We shall again put $b = b_1(1-x) + b_2x$ also in this investigation, and so again disregard the influence of v on the value of b . So from a quantitative point of view our results may be very deficient. But on the other hand it has sufficiently appeared in our former investigation, in which the same approximation was used that the indication of the course of the phenomena obtained in such a way, is correct in the main.

So let us put :

$$\frac{d^2\psi}{dx^2} = MRT \left\{ \frac{1}{x(-x)} + \frac{\left(\frac{db}{dx}\right)^2}{(v-b)} \right\} - \frac{d^2a}{v} = 0$$

and

$$\frac{d^2\psi}{dv^2} = \frac{MRT}{(v-b)^2} - \frac{2a}{v^3} = 0.$$

When we eliminate T from these two equations, we get for the locus of the points of intersection of the two curves :

$$\frac{(v-b^2)}{x(1-x)} + \left(\frac{db}{dx}\right)^2 = v^2 \frac{d^2a}{2a} \dots \dots \dots (a)$$

This locus, in which v occurs in the 2nd degree, and x in the 4th, may present a different shape, and in order to get a survey of the different shapes of this curve, we shall introduce some auxiliary quantities.

These auxiliary quantities will recommend themselves in the discussion of one of the special cases, and for this we choose the case that the whole locus is imaginary for all the values of x between 0 and 1. Let us for this purpose write the equation (a) in the following form :

$$v^2 \left\{ 1-x(1-x) \frac{d^2a}{2a} \right\} - 2bv + \left\{ b^2 + x(1-x) \left(\frac{db}{dx}\right)^2 \right\} = 0 \dots (a')$$

For the case that this locus is imaginary

$$b^2 < \left\{ b^2 + x(1-x) \left(\frac{db}{dx}\right)^2 \right\} \left\{ 1-x(1-x) \frac{d^2a}{2a} \right\}$$

or

$$0 < x(1-x) \left\{ \left(\frac{db}{dx}\right)^2 - \frac{d^2a}{2a} b^2 - x(1-x) \left(\frac{db}{dx}\right)^2 \frac{d^2a}{2a} \right\}$$

or for x between 0 and 1 :

$$0 < \left\{ \frac{\left(\frac{db}{dx}\right)^2}{b^2} - \frac{d^2a}{2a} - x(1-x) \frac{\left(\frac{db}{dx}\right)^2}{b^2} \frac{d^2a}{2a} \right\}$$

or for $\frac{d^2a}{dx^2} = 2(a_1 + a_2 - 2a_{12})$ positive, which we always assume in all our considerations :

$$0 < \frac{a}{a_1 + a_2 - 2a_{12}} - \frac{b^2}{\left(\frac{db}{dx}\right)^2} - x(1-x).$$

If we write :

$$a = a_1 + 2(a_{12} - a_1)x + (a_1 + a_2 - 2a_{12})x^2$$

and

$$b^2 = b_1^2 + 2b_1 \frac{db}{dx} x + \left(\frac{db}{dx}\right)^2 x^2,$$

the latter equation may also be written in the form

$$0 < \left[\frac{a_1}{a_1 + a_2 - 2a_{12}} - \frac{b_1^2}{\left(\frac{db}{dx}\right)^2} \right] + x \left[\frac{2(a_{12} - a_1)}{a_1 + a_2 - 2a_{12}} - \frac{2b_1}{\frac{db}{dx}} - 1 \right] + x^2 \dots (\beta)$$

If we demand that the locus be imaginary all over the width of the figure, so for all the values of x between 0 and 1, there are three conditions :

$$1^{\text{st}} \frac{a_1}{a_1 + a_2 - 2a_{12}} > \frac{b_1^2}{(b_2 - b_1)^2}, \quad 2^{\text{nd}} \frac{a_2}{a_1 + a_2 - 2a_{12}} > \frac{b_2^2}{(b_2 - b_1)^2}$$

and a third condition which is still to be derived.

Let us write for this purpose $a_1 + a_2 - 2a_{12} = c$ and $b_2 = nb_1$, then $1^{\text{st}} \frac{a_1}{c} > \frac{1}{(n-1)^2}$, $2^{\text{nd}} \frac{a_2}{c} > \frac{n^2}{(n-1)^2}$ and when we introduce the

auxiliary quantities ε_1 and ε_2 , so that $\frac{a_1}{c} = \frac{1 + \varepsilon_1}{(n-1)^2}$ and $\frac{a_2}{c} = \frac{n^2(1 + \varepsilon_2)}{(n-1)^2}$

(ε_1 and ε_2 positive), we find from $2a_{12} = a_1 + a_2 - c$ or $\frac{2a_{12}}{2} = \frac{a_1}{c} + \frac{a_2}{c} - 1$

$$2 \frac{a_{12}}{c} = \frac{1 + \varepsilon_1}{(n-1)^2} + \frac{n^2 + n^2 \varepsilon_2}{(n-1)^2} - 1$$

or

$$2 \frac{a_{12}}{c} = \frac{2n + \varepsilon_1 + n^2 \varepsilon_2}{(n-1)^2}.$$

So the condition that this locus be imaginary is that for all the values of x :

$$\frac{\varepsilon_1}{(n-1)^2} - x \left\{ 1 + \frac{\varepsilon_1 - n^2 \varepsilon_2}{(n-1)^2} \right\} + x^2 > 0 \dots \dots (\beta')$$

or

$$\varepsilon_1 > 0 \quad \text{and} \quad \varepsilon_2 > 0 \quad \text{and} \quad 1 + \frac{\varepsilon_1 - n^2 \varepsilon_2}{(n-1)^2} < 2 \frac{\sqrt{\varepsilon_1}}{n-1}$$

The last condition may be written more symmetrically in the form :

$$1 - 2 \frac{\sqrt{\varepsilon_1}}{n-1} + \frac{\varepsilon_1}{(n-1)^2} < \frac{n^2 \varepsilon_2}{(n-1)^2}$$

or

$$1 - \frac{\sqrt{\varepsilon_1}}{n-1} < \frac{n\sqrt{\varepsilon_2}}{n-1}$$

or

$$\sqrt{\varepsilon_1} + n\sqrt{\varepsilon_2} > n-1.$$

So the condition ε_1 and $\varepsilon_2 > 0$ ensures that the locus does not take up the whole width from $x=0$ to $x=1$. For the locus not to exist at all the value of ε_1 and ε_2 must be such that :

$$\sqrt{\varepsilon_1} + n\sqrt{\varepsilon_2} > n-1.$$

If $\sqrt{\varepsilon_1} + n\sqrt{\varepsilon_2} = n-1$, the locus reduces to a single point. In this case :

$$\frac{\varepsilon_1}{(x-1)^2} - x \left\{ 1 + \frac{\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2} \right\} + x^2 = 0.$$

The equation has two coinciding roots, i.e. $x = \frac{\sqrt{\varepsilon_1}}{n-1}$ or $1-x = \frac{n\sqrt{\varepsilon_2}}{n-1}$.

Perhaps these results might have been obtained in a more lucid way, if we had introduced the quantity $N = \frac{x}{1-x}$, instead of x into the equations (a) or (a'), so the number of molecules of the second substance present per molecule of the first substance in the binary mixture, which quantity must necessarily be positive. The condition that the two curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ do not intersect at any temperature assumes then the following form :

$$\frac{\varepsilon_1}{(n-1)^2} - N \left\{ 1 - \frac{\varepsilon_1 + n^2\varepsilon_2}{(n-1)^2} \right\} + \frac{\varepsilon_2 n^2}{(n-1)^2} N^2 > 0. . . (\gamma)$$

For $N=0$ and $N=\infty$ this condition is satisfied for positive ε_1 and ε_2 . But for this equation to be satisfied for any arbitrary value of N it is required that :

$$1 - \frac{\varepsilon_1 + n^2\varepsilon_2}{(n-1)^2} < \sqrt{\frac{4\varepsilon_1 n^2 \varepsilon_2}{(n-1)^2}}$$

or

$$1 < \frac{\varepsilon_1 + n^2\varepsilon_2 + 2\sqrt{n^2\varepsilon_1\varepsilon_2}}{(n-1)^2}$$

or

$$n-1 < \sqrt{\varepsilon_1} + n\sqrt{\varepsilon_2}$$

If we construct the relation between ε_1 and ε_2 as a curve, taking ε_1 and ε_2 as coordinates, we get, for the case that the locus of the points of intersection contracts to a single point :

$$\left\{ 1 - \frac{\varepsilon_1 + n^2 \varepsilon_2}{(n-1)^2} \right\}^2 = \frac{4n^2 \varepsilon_1 \varepsilon_2}{(n-1)^4} \dots \dots \dots (\gamma')$$

and so a parabola. We see from of (γ') that this parabola touches the ε_1 axis and the ε_2 axis in the points of intersection in which the straight line $\frac{\varepsilon_1 + n^2 \varepsilon_2}{(n-1)^2} = 1$ intersects the axes. The equation of this

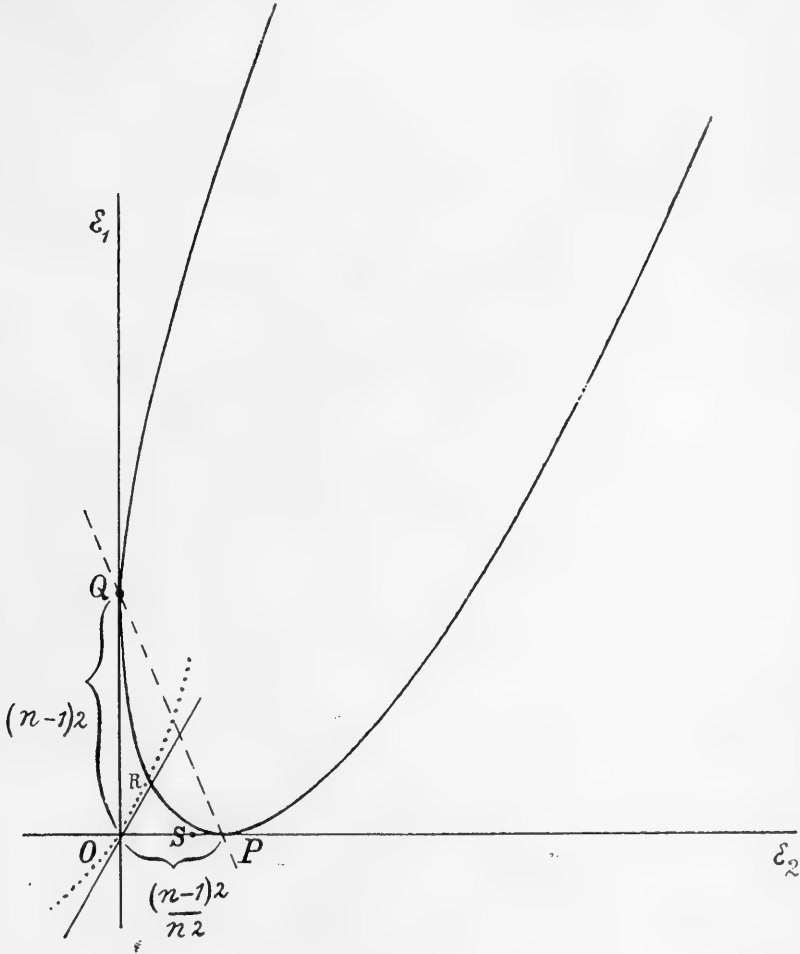


Fig. 36.

parabola may be written in the form $\frac{(\varepsilon_1 - n^2 \varepsilon_2)^2}{(n-1)^4} - 2 \frac{\varepsilon_1 + n^2 \varepsilon_2}{(n-1)^2} + 1 = 0$, from which appears that the direction of the axis or of the diameters of this parabola is given by :

$$\frac{\varepsilon_1}{\varepsilon_2} = n^2,$$

the direction of the above straight line being given by :

$$\frac{\epsilon_1}{\epsilon_2} = -n^2.$$

So these two directions are symmetrical with respect to the axes mentioned. In fig. 36, in which the ϵ_2 axis has been drawn horizontally, the value of n , which is always larger than 1, is not supposed to be very large.

The calculation of the place of the top of the parabola may, among others, be made, by making use of the property that in the top the tangent to the parabola is normal to the direction of the diameter. So $\frac{d\epsilon_1}{d\epsilon_2} = n^2 \frac{\epsilon_1 - n^2\epsilon_2 + (n-1)^2}{\epsilon_1 - n^2\epsilon_2 - (n-1)^2} = -\frac{1}{n^2}$, from which follows that for the top $\epsilon_1 - n^2\epsilon_2 = -(n-1)^2 \frac{n^4-1}{n^4+1}$. This is the equation of the axis; it cuts the ϵ_2 axis in a point in which $\epsilon_1 = 0$ and $\epsilon_2 = OS = \frac{(n-1)^2 n^4 - 1}{n^2 n^4 + 1}$. Hence $OS = OP \times \frac{n^4-1}{n^4+1}$. So for very small values of n also OS is small, but for larger value of n OS approaches to OP .

All the points inside this parabola give values for ϵ_1 and ϵ_2 , for which equation (β) is satisfied; thus this equation reduces for all the points of the line PQ fig. 36 to :

$$\epsilon_1 + \epsilon_2 n^2 N^2 > 0$$

and for sets of values of ϵ_1 and ϵ_2 , belonging to points lying within the parabola, there is, therefore, never intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$.

Summarizing we arrive at the following result. All the points in the positive quadrant of the ϵ_2 , ϵ_1 axes of fig. 36, lying above the line PQ , represent sets of values of ϵ_1 and ϵ_2 , for which (as N must always be positive) no intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ can take place. The points lying below PQ , but within the parabola, also represent such sets. The points below PQ , lying exactly on the parabola represent sets of ϵ_1 and ϵ_2 , for which the locus of the points of intersection of the two curves mentioned reduces to a single point. And finally the points below PQ and below the parabola represent sets of values of ϵ_1 and ϵ_2 for which the two curves yield a locus of points of intersection. The point to which the locus of the points of intersection has contracted lies at a value of

$$N = \frac{x}{1-x} = \frac{1 - \frac{\epsilon_1 + n^2\epsilon_2}{(n-1)^2}}{\frac{n^2\epsilon_2}{(n-1)^2}} = \frac{\sqrt{\epsilon_1}}{n\sqrt{\epsilon_2}}, \text{ at which result we had already}$$

arrived on p. 320, so near $x = 1$, when $n^2\varepsilon_2$ is small compared with ε_1 , and near $x = 0$ when $n^2\varepsilon_2$ may be large compared with ε_1 .

But now we have to consider the question whether such sets of values of ε_1 and ε_2 can actually occur for mixtures. As we do not know any rule as yet which indicates the value of a_{12} for given value of a_1 and a_2 , we cannot give a perfectly decisive answer to this question. But we shall examine what may be derived about this from the rule which is of frequent application:

$$a_1 a_2 > a_{12}^2$$

or

$$n^2(1 + \varepsilon_1)(1 + \varepsilon_2) > \left(n + \frac{\varepsilon_1 + n^2\varepsilon_2}{2} \right)^2$$

or

$$4n^2(1 + \varepsilon_1)(1 + \varepsilon_2) > [(1 + \varepsilon_1) + n^2(1 + \varepsilon_2) - (n-1)^2]^2$$

or

$$4 \frac{n^2}{(n-1)^4} (1 + \varepsilon_1)(1 + \varepsilon_2) > \left[1 - \frac{(1 + \varepsilon_1) + n^2(1 + \varepsilon_2)}{(n-1)^2} \right]^2 \dots (\delta)$$

If we think for a moment the sign $>$ replaced by the sign $=$ the locus (δ) is perfectly equal to (γ) , but with shifting of the two ordinates in the negative direction over an amount equal to -1 . So if we draw two lines, one parallel to the horizontal ε_2 axis at a distance equal to -1 , and one parallel to the vertical ε_1 axis at a distance -1 , and if we construct the same parabola for these two lines, so that also the points P, Q, S are replaced by P', Q', S' , and we have, accordingly, a line $P'Q'$, (δ) is satisfied for all points lying within this parabola.

For the points of the line $P'Q'$ the second member of (δ) is equal to 0 or $a_{12} = 0$, and for the points lying below $P'Q'$ a_{12} would be negative. Accordingly these points will furnish no realizable sets of values of ε_1 and ε_2 . But leaving this for the moment out of consideration, we may say that the series of points which the two parabolas mentioned have in common, fulfil the two requirements that they furnish sets of values of ε_1 and ε_2 which admit of no intersection of $\frac{d^2\psi}{dx^2} = 0$ with $\frac{d^2\psi}{dv^2} = 0$, and for which $a_1 a_2 = a_{12}^2$. This holds equally for the points lying above the first parabola, but within the second. The second parabola enters the positive quadrant of the ε_1 and ε_2 coordinates in the origin, touches there a line $\varepsilon_1 - n\varepsilon_2 = 0$, and so cuts the first parabola in a point represented by R in fig. 36. The equation of the second parabola may, viz. be reduced to the form:

$$(\varepsilon_1 - n^2\varepsilon_2)^2 = 4n(n-1)(\varepsilon_1 - n\varepsilon_2).$$

But if, before drawing conclusions concerning the properties of the components of binary mixtures which admit of no intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$, we consider the meaning of the condition $a_{12}^2 < a_1 a_2$ more closely, it appears that the above remarks should be greatly restricted. Up to now we have been able to draw the conclusion that $a_{12}^2 = a_1 a_2$ leads to a relation between ϵ_1 and ϵ_2 which is graphically represented by what we have called the second parabola, and we have further observed that the condition $a_{12}^2 < a_1 a_2$ leads to values of ϵ_1 and ϵ_2 belonging to points lying within that parabola. According to this view, however, also points lying at infinite distance on or in the neighbourhood of the axis of the second parabola, would furnish sets of values for ϵ_1 and ϵ_2 which might be considered to properly satisfy the condition $\frac{a_{12}^2}{a_1 a_2} < 1$. For these points a_{12}^2 is indeed $< a_1 a_2$, but as well a_1 as a_2 , and a_{12} would be infinitely large for these points, and the ratio of $\frac{a_{12}^2}{a_1 a_2}$ for these points is equal to 1. We get a more accurate limitation of possible values of ϵ_1 and ϵ_2 by putting $a_{12}^2 = l^2 a_1 a_2$ with the condition $l^2 < 1$. So let us put :

$$4l^2 n^2 (1 + \epsilon_1)(1 + \epsilon_2) = (2n + \epsilon_1 + n^2 \epsilon_2)^2. \quad \dots \quad (\delta')$$

or

$$\epsilon_1^2 - 2n^2 \epsilon_1 \epsilon_2 (2l^2 - 1) + n^4 \epsilon_2^2 = 4n \{ \epsilon_1 (l^2 n - 1) - n \epsilon_2 (n - l) - n (1 - l^2) \}$$

This equation represents an ellipse for $l^2 < 1$; for $l^2 = 1$ a parabola and for $l^2 > 1$ a hyperbola. From the form (δ') we see that this locus touches the lines $\epsilon_1 = -1$ and $\epsilon_2 = -1$ in the points in which these lines are intersected by the same line $P'Q'$, which has been mentioned above in the description of the second parabola. If we now again ask if sets of values of ϵ_1 and ϵ_2 are possible belonging to components the binary mixture of which does not admit of intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$, we notice in the first place that

then the ellipse (δ') must intersect the first parabola and the line PQ .

Now, dependent on the value of l^2 in connection with the value of n it is possible that the ellipse remains entirely restricted to negative values of ϵ_2 , in which case intersection with the first parabola is out of the question.

This takes place when the relation between l^2 and n is such that the equation: $4l^2 n^2 (1 + \epsilon_1) = (2n + \epsilon_1)^2$ yields equal or imaginary values for ϵ_1 , and so when:

$$l^2 n^2 \leq 2n - 1$$

holds; for small value of n , e. g. $n = 1,5$, l^2 would have to be $\leq \frac{8}{9}$, which has certainly been found in observations; but for larger values of n , e. g. $n = 5$, l^2 would have to be $< \frac{9}{25}$ which will, most likely, not be the case. So if n is large for a not too small value of l^2 , the ellipse (d') will also possess points for which ε_1 and ε_2 is positive, and the possibility that it intersects the 1st parabola, is not excluded. At given l^2 we might find the limit for the value of n , at which it is still possible that $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ do not intersect, by determining the relation which must exist between l^2 and n for the ellipse to touch the first parabola. But this would lead to lengthy calculations, which we shall omit here. We will, however, examine more closely some properties of the ellipse.

1. Determination of the centre.

From $f'(\varepsilon_1) = 0$ and $f''(\varepsilon_2) = 0$ or $2n + \varepsilon_1 + n^2\varepsilon_2 = 2l^2n^2(1 + \varepsilon_2)$ and $2n + \varepsilon_1 + n^2\varepsilon_2 = 2l^2(1 + \varepsilon_1)$ follows $(1 + \varepsilon_1)M = n^2(1 + \varepsilon_2)M$, from which follows that the line $O'M$ (fig. 37) makes an angle

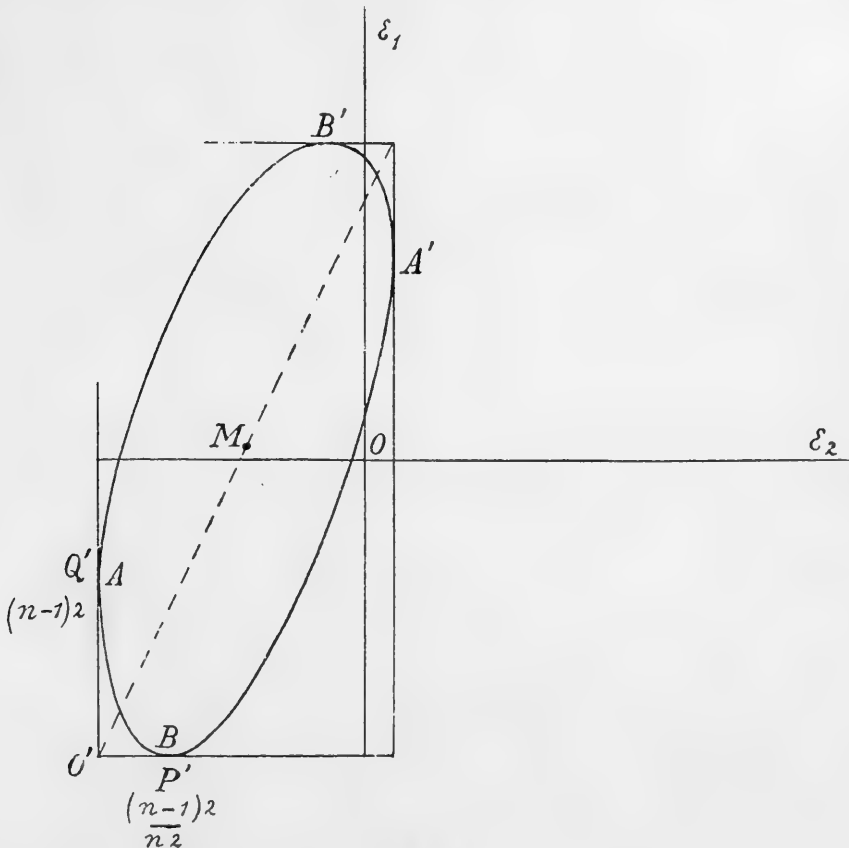


Fig. 37.

with the ε_2 axis, the tangent of which is equal to n^2 , hence $O'M$ is parallel to the axis of the first parabola. For the coordinates of the centre we find:

$$(1 + \varepsilon_1)_M = \frac{(n-1)^2}{2(1-l^2)} \text{ and } (1 + \varepsilon_2)_M = \frac{(n-1)^2}{2n^2(1-l^2)}.$$

2. Highest and lowest point.

For these points $f'\varepsilon_1 = 0$ or

$$-(n-1)^2 + (1 + \varepsilon_1) + n^2(1 + \varepsilon_2) = 2l^2(1 + \varepsilon_1)$$

and so $4l^2n^2(1 + \varepsilon_1)(1 + \varepsilon_2) = 4l^4(1 + \varepsilon_1)^2$.

Hence $1 + \varepsilon_1 = 0$ for the point B and $(1 + \varepsilon_1) = \frac{n^2}{l^2}(1 + \varepsilon_2)$

for the point B' ; from this follows for B' the value $(1 + \varepsilon_1)_{B'} = \frac{(n-1)^2}{1-l^2}$

and $(1 + \varepsilon_2)_{B'} = \frac{l^2}{1-l^2} \frac{(n-1)^2}{n^2}$ and for B is $1 + \varepsilon = \frac{(n-1)^2}{n^2}$.

3. The points A and A' .

For these points $f''\varepsilon_1 = 0$ or

$$-(n-1)^2 + (1 + \varepsilon_1) + n^2(1 + \varepsilon_2) = 2l^2n^2(1 + \varepsilon_2)$$

and so $4l^4n^4(1 + \varepsilon_2)^2 = 4l^2n^2(1 + \varepsilon_1)(1 + \varepsilon_2)$.

Hence for A $1 + \varepsilon_2 = 0$ and $1 + \varepsilon_1 = (n-1)^2$ and for A' holds

$(1 + \varepsilon_1) = l^2n^2(1 + \varepsilon_2)$ or $(1 + \varepsilon_2)_A = \frac{(n-1)^2}{n^2} \frac{1}{1-l^2}$ and:

$$(1 + \varepsilon_1)_{A'} = \frac{l^2}{1-l^2}(n-1)^2.$$

4. The points of intersection with the ε_2 axis.

From $(2n + n^2\varepsilon_2)^2 = 4n^2l^2(1 + \varepsilon_2)$ follows:

$$\varepsilon_2 = \frac{-2(n-l^2) \pm l\sqrt{(n-1)^2 - (1-l^2)}}{n^2}.$$

So while $1-l^2 < (n-1)^2$ there are two points of intersection with the ε_2 axis both on the negative side of the origin. For $l^2 = 1$ one of the points of intersection lies in the origin, and the other point of intersection at $\varepsilon_2 = -4\frac{n-1}{n^2}$, which value = -1 for $n = 2$, and for all other values of n not so large negative. For $1-l^2 = (2-1)^2$ the two points of intersection with the ε_2 axis coincide, and for $1-l^2 > (n-1)^2$ they are imaginary; then the whole ellipse has descended below the horizontal axis. For the case that n is but

little larger than 1, this circumstance is to be expected; then only negative values of ε_1 and ε_2 exist.

5. The intersection with the ε_1 axis.

From $(2n + \varepsilon_1)^2 = 4n^2 l^2 (1 + \varepsilon_1)$ follows:

$$\varepsilon_1 = 2n (nl^2 - 1) \pm 2nl^2 \sqrt{n^2 l^2 - 2n + 1}.$$

For $l^2 = 1$, we get $\varepsilon_1 = 0$ and $\varepsilon_1 = 4n(n-1)$. For $l^2 < 1$ these values approach each other, and they coincide for $l^2 = \frac{2n-1}{n^2}$ as was

stated above. For $l^2 < \frac{2n-1}{n^2}$ or $1-l^2 > \frac{(n-1)^2}{n^2}$ positive values of ε_2

no longer occur. For $l^2 = \frac{3}{4}$ e. g., the ellipse will just touch the ε_1 axis for $n = 2$, and that in a point for which $\varepsilon_1 = 2$; but for smaller value of n the ellipse does not cut the ε_1 axis; for larger value of n , on the other hand, it does.

6. The intersection with the line PQ of fig. 36.

If in:

$$(2n + \varepsilon_1 + n^2 \varepsilon_2)^2 = 4n^2 l^2 (1 + \varepsilon_1)(1 + \varepsilon_2)$$

we substitute the value $\varepsilon_1 + n^2 \varepsilon_2 = (n-1)^2$, we find for the determination of ε_2 , the equation:

$$n^2 \varepsilon_2^2 + 2(n-1)\varepsilon_2 + \frac{(n^2 + 1)^2}{4n^2 l^2} - [1 + (n-1)^2] = 0.$$

When $l^2 < \frac{(n^2 + 1)^2}{4n^2 [1 + (n-1)^2]}$ the two values of ε_2 are negative. If l^2 is greater, a point of intersection is found at positive value of ε_2 ; for l^2 just equal to the given value the ellipse passes exactly through the point Q , and the same relation exists between l^2 and n , as is also found when we substitute the value $(n-1)^2$ for ε_1 in the equation of 5.

While one of the values of ε_2 is positive the ellipse intersects not only the line PQ , but also the first parabola. For smaller value of l^2 or larger of n , the line PQ is no longer intersected in the positive quadrant; intersection of the ellipse with the first parabola will, indeed, be still possible, till the two points of intersection coincide with further decrease of l^2 . Then the ellipse touches the parabola, and the possibility that $\frac{d^2 \psi}{dx^2} = 0$ and $\frac{d^2 \psi}{dv^2} = 0$ no longer intersect, vanishes.

7. Another form for the equation of the ellipse.

Most of the above results may be obtained by considering that the equation of the ellipse may also be written in the form:

$$\left\{ (1 + \varepsilon_1) + n^2(1 + \varepsilon_2) - \frac{1 + l^2}{1 - l^2}(n-1)^2 \right\}^2 = 4n^2 l^2 \left\{ 1 + \varepsilon_1 - \frac{(n-1)^2}{1 - l^2} \right\} \left\{ 1 + \varepsilon_2 - \frac{(n-1)^2}{n^2} \frac{1}{1 - l^2} \right\}.$$

The first member put equal to 0 is the equation of the line $A'B'$, and the factors of the second member put equal to 0 are the equations of tangents to the ellipse in the points B' and A' .

If the ellipse intersects the first parabola, and so also twice the ε_1 axis, and if therefore part of the ellipse lies within the first parabola, then there is a continual series of points which yield sets of values of ε_1 and ε_2 for which no three-phase-pressure is to be expected. This series of points begins where the ellipse cuts the first parabola in the 1st or lowest point, and terminates either in the second point of intersection or in the ε_1 axis. In the latter case when the second point of intersection with the ε_1 axis lies higher than $(n-1)^2$.

8. Ratio of the critical temperatures of the components.

For a point of the ellipse is $\frac{a_1}{c} = \frac{1 + \varepsilon_1}{(n-1)^2}$ and $\frac{a_2}{c} = \frac{n^2(1 + \varepsilon_2)}{(n-1)^2}$, and so

$\frac{T_{k_2}}{T_{k_1}} = \frac{n(1 + \varepsilon_2)}{1 + \varepsilon_1}$. If from the point O' ($\varepsilon_1 = -1$ and $\varepsilon_2 = -1$) we draw a line to such a point, and if we put the angle which this

line makes with the ε_2 axis equal to φ , then $\frac{1 + \varepsilon_1}{1 + \varepsilon_2} = \tan \varphi$, and so

also $\frac{T_{k_2}}{T_{k_1}} = n \cot \varphi$ or $\tan \varphi = n \frac{T_{k_1}}{T_{k_2}}$. If we put the question whether all

the points of the ellipse can occur, we notice first of all that the condition $a_{12} > 0$ already excludes the points lying below the line $P'Q'$. Let the ellipse be inclosed in a rectangle, the sides of which are parallel to the axes, let us draw the diagonal through the centre for which $\tan \varphi = n^2$ from the point O' ($\varepsilon_1 = -1$ and $\varepsilon_2 = -1$).

This diagonal cuts the ellipse in a point that belongs to $\frac{T_{k_2}}{T_{k_1}} = \frac{1}{n}$.

For all the points of the ellipse lying right of this point, $\tan \varphi > n^2$,

and so $\frac{T_{k_2}}{T_{k_1}} < \frac{1}{n}$. Thus we should have $\frac{T_{k_2}}{T_{k_1}} = \frac{l^2}{n}$ for the highest point

of the ellipse. We cannot assert with any certainty that such cases do not occur. Substances with larger molecules have not a necessarily higher T_k , and that the critical temperature can be lower with $n > 1$

we have assumed as possible among others in the course of the isobars.

When we take into account mixtures of water and other substances, we find this frequently to be the case. Thus for water and ether n is about 5 and $(T_k)_{ether} = \text{about } \frac{3}{4} (T_k)_{water}$. For water and CO_2

$n = 2,5$ and $\frac{T_{k_2}}{T_{k_1}} = \frac{304}{638}$. For water and nitrogen $n = 1,6$ and $\frac{T_{k_2}}{T_{k_1}}$ much smaller than $\frac{1}{n}$. But it still remains an open question in how

far our theory may be applied in unmodified form for mixtures of which one of the components is *water*, a substance which behaves so abnormally. In any case it is only by way of exception that points of the ellipse lying on the left of the diagonal, are of practical importance. If we now proceed to consider points right of the diagonal we mention in the first place the point in which the ellipse is cut by a line from O' , and for which $tg \varphi = n$. For this point $\frac{T_{k_2}}{T_{k_1}} = 1$. For all the points for which $tg \varphi$ lies between n^2 and n $T_{k_2} < T_{k_1}$. But for points for which $tg \varphi < n$, $T_{k_2} > T_{k_1}$. So mixtures of substances for which the substance with the larger molecule has also the higher critical temperature are represented by those points of the ellipse for which $tg \varphi < n$, whereas, if $tg \varphi = 1$, we have the case that the critical pressures are the same. For this value of $\frac{p_{k_2}}{p_{k_1}}$ is equal to $\frac{1 + \epsilon_2}{1 + \epsilon_1}$. So the points for which $\frac{1 + \epsilon_1}{1 + \epsilon_2} < 1$ represent mixtures for which the substance with the larger molecule has not only higher critical temperature, but also higher critical pressure. Such lines intersect the ellipse in points in which both ϵ_1 and ϵ_2 is negative, and as it is required for non-intersection of $\frac{d^2 \eta}{dv^2} = 0$ and

$\frac{d^2 \eta}{dv^2} = 0$ that these quantities are positive, and lie even beyond the line FQ , the rule would follow that for mixtures of substances for which the substance with the larger molecule has the greater critical pressure three-phase-pressure must occur. If experience should refute this, i.e. if it should appear that for mixtures of such substances absence of three-phase-pressure can be found, we should be induced to put the question: Is perhaps in some cases

$$a_{12}^2 > a_1 a_2$$

possible; then in the equation (d') viz.:

$$4l^2 n^2 (1 + \epsilon_1)(1 + \epsilon_2) = \{2n + \epsilon_1 + n^2 \epsilon_2\}^2$$

the quantity l^2 is > 1 , and this equation represents a hyperbola.

For $l^2 > 1$ the two points of intersection with the ϵ_2 axis lie on the negative side of the origin. For $l^2 = 1$ one of the points of intersection has got into the point O , and for $l^2 > 1$ one of the points of intersection lies on the righthand side of O , so at a value of ϵ_2 which is positive. The branch of the hyperbola passing through this point, then intersects the first parabola and the line PQ , or only the first parabola; a line $\frac{1 + \epsilon_1}{1 + \epsilon_2} < 1$ can then cut the hyperbola in points for which ϵ_1 and ϵ_2 are positive, and then absence of three-phase-pressure may again be expected.

But let us return to the examination of the equation (a) after our digression. Till now we have discussed the condition on which this equation has no real root. Let us now pass to other possible cases. The roots of this equation have the form:

$$\frac{v}{b} = \frac{1 \pm \sqrt{\left\{ 1 - \left[1 - x(1-x) \frac{c}{a} \right] \left[1 + x(1-x) \frac{\left(\frac{db}{dx}\right)}{b^2} \right] \right\}}}{1 - x(1-x) \frac{c}{a}}$$

or

$$\frac{v}{b} = \frac{1 \pm \sqrt{x(1-x) \frac{c}{a} \frac{\left(\frac{db}{dx}\right)^2}{b^2} - \frac{\epsilon_1}{(n-1)^2} + x \frac{\epsilon_1 - n^2 \epsilon_2}{(n-1)^2} + x(1-x)}}{1 - x(1-x) \frac{c}{a}}$$

We shall continue to suppose the denominator to be positive. For $x=0$ the expression under the radical sign is equal to $-\frac{\epsilon_1}{(n-1)^2}$ and for $x=1$ equal to $-\frac{n^2 \epsilon_2}{(n-1)^2}$, and for these values $\frac{v}{b}$ is, therefore, imaginary for positive ϵ_1 and ϵ_2 . Now we put $\sqrt{\epsilon_1} + n\sqrt{\epsilon_2} > n-1$ before; this supposition implies that $\frac{v}{b}$ is imaginary all over the width from $x=0$ to $x=1$. Let us now put $\sqrt{\epsilon_1} + n\sqrt{\epsilon_2} < n-1$.

Then the equation $-\frac{\epsilon_1}{(n-1)^2} + x \frac{\epsilon_1 - n^2 \epsilon_2}{(n-1)^2} - x(1-x) = 0$ has two roots for x between 0 and 1. For these definite values of $x \frac{v}{b}$ has

two equal values. For x outside these values $\frac{v}{b}$ is imaginary, and within these limits two positive values of $\frac{v}{b} > 1$ satisfy. That $\frac{v}{b} > 1$ or $\frac{v-b}{b}$ is positive may among others be seen when we have developed the equation (a) as quadratic equation in $(v-b)$. The two real values of $\frac{v-b}{b}$ are both positive, if $\frac{\left(\frac{db}{dx}\right)^2}{b^2} > \frac{c}{a}$; and the equation in x requires that this condition is fulfilled for real values of $\frac{v}{b}$. From this follows that if the conditions $\varepsilon_1 > 0, \varepsilon_2 > 0$ and $\sqrt{\varepsilon_1 + n\sqrt{\varepsilon_2}} < n-1$ are fulfilled the locus of the points of intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ is a closed figure. The limiting values for $N = \frac{v}{1-x}$ have been given (see formula (y)) by :

$$\frac{\varepsilon^1}{(n-1)^2} - N \left\{ 1 - \frac{\varepsilon^1 + n^2 \varepsilon_2}{(n-1)^2} \right\} + N^2 \frac{n^2 \varepsilon_2}{(n-1)^2} = 0.$$

For these values of x , the volumes for a given value of x have coincided, and are equal to $\frac{b}{1-x(1-x)\frac{c}{a}}$. The existence of such a closed figure with volumes larger than b means that at exceedingly low temperature the two curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ do not intersect. Not before a certain value of T e.g. T_1 these two meet. At the lower temperatures the whole curve $\frac{d^2\psi}{dx^2} = 0$ lies in the space where $\frac{d^2\psi}{dv^2}$ is negative. At T_1 the branch of the small volumes of $\frac{d^2\psi}{dv^2} = 0$ has overtaken the branch of the small volumes of $\frac{d^2\psi}{dx^2} = 0$. At $T > T_1$ part of $\frac{d^2\psi}{dx^2} = 0$ lies in the region where $\frac{d^2\psi}{dv^2}$ is positive. But with further rise of the temperature a change is brought about in the relative movement of the two curves inter se, and at certain temperature equal to T_2 the branches of the small volumes of the

two curves meet again; and at still higher temperature $\frac{d^2\psi}{dx^2} = 0$ lies again entirely within $\frac{d^2\psi}{dv^2} = 0$. Then three-phase-pressure is to be expected between two temperatures, whose values though not coinciding with T_1 and T_2 , are yet in close connection with these values. But for this I refer to previous papers.

The two values of x , between which the locus of the points of intersection $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ is contained, lie in general not symmetrically with respect to $x = 0$ and $x = 1$. Let these values be denoted by x_1 and x_2 , then:

$$x_1 + x_2 = 1 + \frac{\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2}$$

or if the value of x , which lies halfway between them is called x_m :

$$2x_m = 1 + \frac{\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2}.$$

So if $\varepsilon_1 > n^2\varepsilon_2$, then $x_m > \frac{1}{2}$ and vice versa. This remark may contribute to the solution of the question whether for mixtures for which three-phase-pressure exists between two temperatures T_1 and T_2 , the quantity $l^2 > 1$ or < 1 . If $l^2 < 1$, and if, therefore, the points for which ε_1 and ε_2 are the coordinates, can but lie on an ellipse which can only enter the space between the ε_1 and ε_2 axis and the first parabola in a point $\varepsilon_1 > 0$ and $\varepsilon_2 = 0$, then $x_m > \frac{1}{2}$ may be expected. On the other hand if $l^2 > 1$, and the considered points lie on a hyperbola, $\varepsilon_2 > 0$ and $\varepsilon_1 < n^2\varepsilon_2$ is to be expected. Then the discussed locus lies on the side of the component of the smallest size of the molecules — which occurs for mixtures of ethane and alcohols. For the case $\varepsilon_1 = 0$ and $n^2\varepsilon_2 > 0$, $x_1 = 0$ and $x_2 = 1 - \frac{n^2\varepsilon_2}{(n-1)^2}$. But $x_1 = 0$ for $v - b = 0$, from which follows at the same time $T_1 = 0$, so there is in this case three-phase-pressure at all temperatures below T_2 . In the same way the value of T_1 would be equal to zero for $\varepsilon_2 = 0$ and $\varepsilon_1 > 0$.

In all this it must not be overlooked that though the presence or absence of three-phase-pressure is, indeed, closely connected with the presence or absence of the locus of the points of intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$, there are differences to be expected in the particulars. Thus the temperatures for the limits between which three-phase-pressure can be observed, are not the same as we have denoted

by T_1 and T_2 . First of all on account of the theoretical existence of *hidden* three-phase-pressure; but also because the presence or absence of a hidden plaitpoint does not coincide with the intersection or non-intersection of $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$. Moreover the existence of the liquid state is also assumed here for all temperatures, however low. The occurrence of the solid state may, of course, be a hindrance for the observation of what we have called the temperature T_1 . Thus in mixtures of water and phenol an utmost temperature limit has been found for three-phase-pressure; but it is still an open question whether there also exists a lowest temperature, higher than the absolute zero point.

(*To be continued*)

Physics. — “*On the measurement of very low temperatures. XXI.*

On the standardizing of temperatures by means of boiling points of pure substances. The determination of the vapour pressure of oxygen at three temperatures.” By Dr. H. KAMERLINGH ONNES and Dr. C. BRAAK. Communication N^o. 107^a from the physical laboratory at Leiden.

(Communicated in the meeting of May 30, 1908).

§ 1. *Introduction.* In a preceding Communication N^o. 101^a (Dec. '07) we have spoken of the desirability of determining once for all certain temperatures by means of boiling point apparatus, because the points of the temperature scale thus fixed have the advantage over those fixed with resistance thermometers and thermo-elements that they do not depend on the durability of special apparatus and they facilitate comparisons between thermometers in different laboratories.

This Communication treats of a number of determinations with oxygen: *a.* a little above and a little below the normal boiling point from which the latter could be derived; *b.* at 366 and 516 mm. mercury pressure which may serve to give information about the further course of the vapour pressure curve.

After some preliminary determinations we have constructed two apparatus of different dimensions, in each of which different quantities of gas could be successively condensed. Thus we have obtained two series of independent determinations; at the same time the purity of the gas could be tested.

§ 2 *The measuring apparatus.* (See Pl. I).

In the vapour pressure apparatus of the small pattern *A* about 120 cc. gas can be condensed, in the large pattern *B* about 1 Liter. Pattern *A* consists of a bulb *a* of 0.5 cc. with a glass stem *b*, connected to a manometer with a steel capillary *c*. The manometer consists of two tubes m_1m_2 of 2 cm. bore filled with mercury; they are connected by an india rubber tube. An air-trap *d* prevents impurities from coming into the gas. The glass stem is moreover surrounded by a copper cylinder *e* and a glass jacket *f* by means of which heat is conducted from above, thus preventing the temperature at any part of the apparatus from falling below that of the bulb which is placed in the cryostat at the place where the temperature is measured. By pressing the mercury higher up or lower down one can condense different quantities of gas successively.

The construction of pattern *B* differs a little from that of *A*; this is especially in order to avoid the apparatus becoming difficult to handle because a too large quantity of mercury would be required. The manometer m_1m_2 consists of a *U*-tube of glass of which the two limbs are separated by a glass cock k_1 . This *U*-tube is blown on to another d_1d_2 which contains the gas. The two limbs of the latter are cylinders of 70 c.m. length and 0.5 liter contents separated by a cock k_2 . The limb d_1 connected to the manometer is fixed at its upper end to the steel capillary *c* which is connected with the bulb *a*. The limb d_2 carries a glass cock k_3 , through which the apparatus is filled. The reservoir is filled to 1 atm. excess of pressure with gas. By first shutting k_3 and then opening it we can condense first the gas of d_1 which is under an excess of pressure, then also that of d_2 .

A enables us to judge of the purity of the gas when we investigate in how far the vapour pressure measured depends on the fraction of the quantity of gas already condensed. By means of *B*, where the quantity of condensed gas always amounts to the same portion of the total quantity, we can determine in how far the vapour pressure is independent of the increase or decrease of the quantity of the condensed gas itself.

The oxygen is prepared from potassium permanganate through heating. After it has been carefully purified and dried over a KOH-solution and P_2O_5 , the gas is condensed in a bulb immersed in liquid air. Then the liquid air is removed and the apparatus are filled with the evaporated gas.

The pressure was read with a cathetometer; this does not require a very high degree of accuracy because of the great variability of

the vapour pressure with the temperature. The atmospheric pressure on the mercury in the open manometer was read on an aneroid, barometer which we occasionally compared with a mercury barometer.

§ 3. *The determination of temperature and the degree of accuracy.*

For measuring the temperature we have used for the determinations in the neighbourhood of the boiling point of oxygen the resistance thermometer Pt'_I which has been compared ¹⁾ (comp. Comms. N^o. 95^c Sept. '06 and N^o. 101^a Dec. '07) over a large range with the hydrogen thermometer of Comm. N^o. 95^e (Oct. '06) which we shall call B_{III} ; for -182° this was done on March 25th 1907 (comp. Comm. N^o. 101^a table I). Some calibrations have afterwards been made, which together with those just named are given in table II. This table also contains the results of an indirect comparison of Pt'_I with another hydrogen thermometer, which we call T_4 and which was used in an investigation of Dr. FEUSTEL and one of us (K. O.) with a differential thermometer helium-hydrogen, which investigation will soon be published.

In connection with § 4 of Comm. N^o. 101^a we have also given in table I the results of 4 comparisons between two resistance thermometers Pt'_I and Pt''_d ³⁾ at about -183° C. and -217° C.

TABLE I. Comparison between Pt'_I and Pt''_d .

Date	Pt'_I	Pt''_d	Pt'_I and Pt''_d in degrees
22 June '07	34.267	18.565 ³⁾	0 ^o .000
18 Dec. '07	34.359	18.609	
24 June '07	14.761	9.1483 ³⁾	0 ^o .007
19 Dec. '07	14.824	9.1793	

For the measurements on 18th and 19th Dec. '07 B_{III} , Pt'_I and

¹⁾ $W_{PtI} = 1.01806 W_{PtI}$ (comp. § 2 of Comm. N^o. 101^a Dec. 1907).

²⁾ This resistance thermometer is the same as the one which in Comm. N^o. 99^b (Sept. '07) is called Pt'_d . Afterwards it has broken in the middle, and consequently the resistance was diminished to half its value (Pt''_d). Here it is indicated with two accents because it has then undergone a small reparation owing to which $Pt''_d = 1.00073 Pt'_d$ at 0° .

³⁾ This value has been reduced with the factor of the preceding footnote.

Pt''_d were placed in the cryostat. Thus we simultaneously obtained the results relating to them of the tables I and II. Those of the second part of table II are derived from a comparison between Pt''_d and T_4 . The resistances observed were reduced with the factor 1.00073 (cf. the footnote on the preceding page), giving 18.560 and 18.398 Ω . These have been reduced with the data of table I to Pt'_I . This yields the values of the third column.

The calibration of T_4 agrees satisfactorily with that of B_{III} . The mean of the deviations for the two former and the two latter data differs from table II by 0.022 Ω which corresponds to $0^\circ.038$. This small difference between the readings of two entirely different gas thermometers satisfactorily confirms the exactness of the limit of accuracy derived formerly (Comm. N^o. 95^e) and enhances the reliability of the other preceding determinations of temperature.

TABLE II. Comparison of the resistance thermometer Pt'_I with the hydrogen thermometers B_{III} and T_4 .

Comparison with B_{III}			
Date	Temperature according to the hydrogen thermom. B_{III}	Resistance in Ω	${}^0Pt'_I - C_{A_I}$
25 March '07	— 182 ^o .352	34.492	— 0.008
18 Dec. '07	— 182 ^o .595	34.359	— 0.000
17 Febr. '08	— 186 ^o .590	32.027	— 0.019
18 Febr. '08	— 189 ^o .500	30.332	— 0.041
19 Dec. '07	— 216 ^o .840	14.824	+ 0.031
Comparison with T_4			
30 Nov. '07	— 182 ^o .736 ¹⁾	34.257	— 0.021
3 Dec. '07	— 183 ^o .302 ¹⁾	23.919	— 0.031

¹⁾ The hydrogen thermometer temperatures are calculated on the scale of Comm. N^o. 95^e (Oct. '06). As the zero pressure amounted to about 1360 mm. we have accordingly accepted for the coefficient of pressure variation 0.0036629, derived from the coefficient of pressure variation of Comm. N^o. 60 (Sept. 1900) (0.0036627 for 1100 mm. zero pressure). We have also applied a correction according to the difference of the correction to the absolute scale for 1360 and 1100 mm. zero pressure.

The tables I and II also give new data about the accuracy of the readings of the resistance and of the gas thermometer¹⁾. According to table I the error of the resistance remains below 0.°01. As to the readings of the gas thermometer, the first two data of table II inter se yield a difference smaller than 0.°02. With the difference + 0.031 Ω at -217° correspond + 0,028 and + 0.016 of table II in Comm. N°. 95^c and table I in Comm. N°. 101^a. This also agrees with the accuracy of 0.°02 derived in § 7 of Comm. N°. 95^c. This seems not to be the case for the value of 18 Febr. '08 which deviates rather much from the formula. It will depend on later determinations what part of this deviation must be ascribed to the formula AI .

§ 4. *The vapour pressure determinations in the neighbourhood of the boiling point of oxygen.*

We have used the cryostat described in Comm. N°. 94^f (Pl. V) (Sept. 1906). The temperature was determined and regulated with the resistance Pt'_I placed in the bath. The deviations of the galvanometer were so small that no correction was required for it. In the apparatus A the mercury was raised successively in the lower and the upper end of the manometer m_1 , in B first the gas of one reservoir was condensed, afterwards of the two reservoirs. This is indicated in the following table with "little" and "much". Table III contains a determination at a small excess of pressure, another at a pressure of a little below 760 m.m. and a determination for control also at an excess of pressure. The pressure is reduced to 0° C. The last column contains the deviations from the mean for each series.

The resistances of the thermometer read on the WHEATSTONE bridge were for the three series respectively:

$$34.433 \quad , \quad 34.098 \quad \text{and} \quad 34.433 \quad \Omega.$$

If we compare the results obtained with the condensation of a little quantity of gas with those with the condensation of a large quantity we cannot find any systematical deviations, which speaks for the purity of the gas used. In case impurities should occur their influence on the vapour pressure derived with the smaller condensation is sure to be less than the influence on the difference just mentioned. It may therefore be neglected.

¹⁾ Comp. Comms. No. 95^c, 95^e and 101^a.

TABLE III. Vapour pressure of oxygen in the neighbourhood of the boiling point.

Date	Time		Pressure in m.m. mercury	Mean of a series	Deviation from the mean
6 Febr. '08 excess of pressure Series I	h 4 31'	large pattern (little)	806.34	806.71	-0.37
	4 46	small " (much)	806.55		-0.16
	5 0	" " (little)	806.98		+0.27
	5 8	large " (much)	806.97		+0.26
7 Febr. '08 pressure a little below 760 mm. Series II	10 13	small " (little)	759.47	759.61	-0.14
	10 21	" " "	759.75		+0.14
	10 50	" " (much)	759.46		-0.15
			759.54		-0.07
	11 12	large " "	759.35		-0.26
			759.51		-0.10
	11 47	" " "	759.76		+0.15
12 26	small " (little)	759.84	+0.23		
12 37	large " (much)	759.82	+0.21		
7 Febr. '08 excess of pressure Series III	1 20	small " (little)	806.17	806.26	-0.09
	1 25	large " (much)	806.30		+0.04
	1 35	small " (little)	806.31		+0.05

§ 5. Accuracy of the adjustments.

From the results of table III we derive the following data.

The deviations from the mean which must be ascribed partly to the regulation of the temperature are small and when reduced to differences of temperature they remain below $0^{\circ}.005$.

The mean of the results of the large and the small pattern derived separately for each series gives:

Series I, large pattern	$p = 806.65$	(2 observations)
small " "	806.76	(2 ")
Series II, large " "	$p = 759.64$	(5 ")
small " "	759.58	(4 ")
Series III, large " "	$p = 806.30$	(1 observation)
small " "	806.24	(2 observations)

The difference between the two means is at the utmost 0.1 mm. which corresponds to $\frac{1^\circ}{800}$. Thence we may conclude that a vapour pressure apparatus is extremely suited for the standardizing of temperatures. The data obtained here show that in this respect the apparatus surpasses the gas thermometer and probably also the resistance thermometer. For the hydrogen thermometer, namely, the error of 2 adjustments amounts to 0.01 à 0°.02 (comp. § 3 and Comm. N°. 95^c § 8 and N°. 101^a § 3), for the resistance thermometer to 0°.01 (comp. § 3 and Comm. N°. 101^a § 4¹).

§ 6. *The determination of the boiling point of oxygen.*

With the resistances of Pt_1 given in § 4 we can by means of the data of table II derive the corresponding temperatures on the scale of our hydrogen thermometer B_{III} . To this end we start from the mean of the two data of March 25 and Dec. 18, '07, because these are probably more accurate than those obtained with the thermometer T_4 . To 34.433 and 34.098 Ω correspond the temperatures $-182^\circ.460$ and $-183^\circ.040$ respectively. To the first belongs the vapour pressure 806.40 m.m. (the mean from the series I and III) to the second 759.61 mm. (series II). Thence follows by means of rectilinear interpolation for 760 mm. at Leiden for the temperature on the thermometer B_{III} : $t = -183^\circ.035$ and for the normal boiling point (760 mm. on sea-level and 45° northern latitude):

$$t = -183^\circ.030 - 0^\circ.007 = -183^\circ.037$$

on the normal hydrogen thermometer and (comp. table XXV of Comm. N°. 101^b Dec. 1907)

$$\theta = -183^\circ.042 + 0^\circ.056 = -182^\circ.986$$

on the absolute scale.

If we take into consideration the degree of accuracy of the correction to the absolute scale (comp. Comm. N°. 97^b March '07) and the results for the control determinations for the measurement of temperature made as well with the same hydrogen thermometer as with different ones, then it follows that this value does not probably deviate from the real value by more than 0°.03.

1) The data of table III also enable us to judge of the accuracy of the adjustment of the resistance. Let the error in the reading of vapour pressure apparatus = 0, which approximately is permissible according to what precedes, then the difference of the means for the series I and III must be ascribed to the error of the measurement of the resistance. This then would be 0°.005.

§ 7. *Vapour pressure determination at lower temperatures.*

For these measurements (comp. § 2 table II) the temperature was directly read on the hydrogen thermometer *B_{III}*; *Pt_I* was used for the regulation. The temperatures are $-186^{\circ}.599$ and $-189^{\circ}.500$ (comp. table II). At the same time we obtained a new calibration for *Pt_I*. The determinations were made with only the small vapour pressure apparatus. The results are combined in table IV in the same way as in table III.

In the determinations marked (a) about half of the gas was condensed, in those marked (b) about $\frac{4}{5}$ of the gas. As was the case for the boiling point no systematic difference resulting from this seems to be perceptible. If we reduce the temperatures to the absolute scale and the pressures to sea-level and 45° northern latitude we find for:

$$\begin{aligned} \theta &= -186^{\circ}.542 & p &= 516.19 \text{ mm.} \\ \theta &= -189^{\circ}.442 & p &= 366.24 \text{ mm.} \end{aligned}$$

TABLE IV. Vapour pressure of oxygen below the boiling point.

Date	Time	Pressure in mm.	Mean of a series	Deviation from the mean
17 Febr. '08	(a) 2 55'	366.06	365.99	+0.07
	(a) 3 30	365.90		-0.09
	(b) 4 5	366.00		+0.01
	(b) 4 25	365.98		-0.01
18 Febr. '08	(a) 10 42	515.82	515.83	-0.01
	(a) 11 6	515.89		+0.06
	(b) 11 30	515.69		-0.14
	(b) 11 40	515.94		+0.11

§ 8. *The results compared with those of other observers.*

Of previous determinations those by TRAVERS, SENTER and JAQUEROD¹⁾ deserve most confidence, especially because these observers used pure oxygen in a closed reservoir. This is not the case with

¹⁾ Phil. Trans. Roy. Soc. Series A. Vol. 200, 1902

the other observations where the temperature of a bath of oxygen boiling under atmospheric pressure was determined. For then impurities, nitrogen as well as less volatile substances are unavoidable. It seems that the influence of the latter is paramount; all these results for the boiling point are too high by $0^{\circ}.3$ or more. The first mentioned determinations yield for the boiling point of oxygen $-182^{\circ}.93$ on the normal hydrogen scale. For the pressure 760 mm. is given without indication of a further reduction. Our value for 760 mm. mercury (at 0°) is on the normal hydrogen scale $-183^{\circ}.030$, differing by $0^{\circ}.10$ from the value mentioned above. One of the last determinations is that of GRUNMACH ¹⁾. He finds $-182^{\circ}.23$. With the correction derived by HOFFMANN and ROTHE ²⁾ for the pentane thermometer ($-0^{\circ}.42$) this becomes $-182^{\circ}.66$, a result which after being corrected is still much too high.

If we compare the two observations at lower pressure with those of TRAVERS, SENTER and JAQUEROD then it appears that both our temperatures are lower by $0^{\circ}.13$. Hence it is clear that a systematic difference exists between the two series.

¹⁾ Berliner Sitz. Ber. 1906.

²⁾ Zeitschr. f. Instrkd. 27. 1807.



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday November 28, 1908.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige
Afdeeling van Zaterdag 28 November 1908, Dl. XVII).

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Physics. — “*On the measurement of very low temperatures. XXII. The thermo-element gold-silver at liquid hydrogen temperatures.*”
By H. KAMERLINGH ONNES and J. CLAY. (Communication N^o. 107^b from the physical laboratory at Leiden).

(Communicated in the meeting of May 30, 1908).

The thermo-element gold-silver of which, when one of the limbs is kept at 0°, the electromotive force at ordinary temperature is about zero, shows at lower temperatures a more and more rapid increase of electromotive force¹⁾.

A calibration with the hydrogen thermometer has shown that at the temperatures which can be reached with liquid and solid hydrogen the increase of the electromotive force of this thermo-element per degree becomes large enough to render it suitable for temperature determinations in the area under consideration, while at the temperatures far below the melting point of hydrogen (for the determination of which the helium thermometer must be used for the calibration instead of the hydrogen thermometer) the sensibility of the instrument will be greater still.

The following table may serve to make this clear.

TABLE I. Calibration of the thermo-element gold-silver at hydrogen temperatures.

Temperature read on the hydrogen thermom.	Electromotive force in millivolts.	
	gold-silver	(constantin-steel)
(-216.01)	(0.11972)	
(-217.416)		(6.8310)
-252.86	0.24742	
-252.93		(7.1315)
-255.34	0.26304	
-258.61	0.28912	
-259.24		(7.1585)

¹⁾ Comp. the measurements of J. CLAY in his thesis for the doctorate and in Comm. no. 107^d from the Physical Laboratory at Leiden.

The third column contains the determinations about the element constantin-steel of Table VI in Comm. N^o. 95^a (Sept. '06). Owing to the great lessening of the increase of the electromotive force per degree this element is unfit for the accurate measurement of the lowest temperatures¹⁾.

We shall soon publish a calibration of the thermo-element gold-silver with the helium thermometer at low temperatures.

Physics. — “*On the change of the resistance of pure metals at very low temperatures and the influence exerted on it by small amounts of admixtures.* II. By H. KAMERLINGH ONNES and J. CLAY. Communication N^o. 107^c from the physical laboratory at Leiden.

(Communicated in the meeting of May 30, 1908).

§ 7. *Supplementary notes to Comm. N^o. 99^c* (Sept. '07). We add to it with regard to²⁾:

Gold. A formula of the form D has been derived for Au_{17} . The drawing thinner of gold wire has the same influence as we remarked in the comparison of the thin wire Pt_d with Pt_I in Comm. N^o. 99^b (Sept. '07) which influence was ascribed to impurities. With two gold wires it was possible by means of analysis to show the difference in composition called forth by drawing.

Mercury. The values given in Comm. N^o. 99^c are represented (except at 0°) by the quadratic formula.

$$W_t = 22.3605 (1 + 0.00358 t - 0.06588 t^2)$$

which for $-197^{\circ}.87$ gives $O - C = +0.0106$ so that we are led to think that the temperature has not been observed quite accurately enough. Of the metals investigated it seems that mercury is best suited for the measurement of temperatures below the meltingpoint of hydrogen.

Lead. For lead two formulae were derived of the form A' and B' (A and B each time with omission of the term $c \left(\frac{t}{100} \right)^3$), according

¹⁾ Also the element german silver-platinum investigated by DEWAR (Proc. Roy. Soc. ser. A, vol. 76 p. 316 sqq. 1905) is unfit for this purpose because of the same fault.

²⁾ Observations, formulae and other details are given in J. CLAY's thesis for the doctorate, and in Comm. N^o. 107^c for the sections 7 and 8, in Comm. N^o. 107^d for § 9.

to which we must reject the observation at $-255^{\circ}.07$ yielding 0.02314 where A' gives 0.01974 and B' 0.01984.

§ 8. *Carbon and constantin.* Besides the variations of the metals investigated we have ¹⁾ also investigated to -262° the variations of resistance of carbon and constantin.

§ 9. *Alloys of Au and Ag.* One of us (J. CLAY) has extended the investigation treated of in the preceding sections to different alloys of gold and silver and has added the determination of the electromotive force of the thermo-element gold-silver. This investigation showed that the theories of RAYLEIGH and LIEBEXOW about the thermo-electric origin of the difference in resistance introduced in § 1 (the additive resistance of MATTHIESEN ²⁾), must be rejected. For the value p , introduced in § 1, the observations mentioned yield with a gold wire of 1 m. in length and 1 mm.² in section per volume percent silver added

$$p = 0.00360 \Omega.$$

Mathematics. — “*On certain twisted sextics*”. By Mr. M. STUYVAERT at Ghent. (Communicated by Prof. JAN DE VRIES).

(Communicated in the meeting of October 31, 1908).

Prof. JAN DE VRIES has had the goodness to send us an interesting paper which he has published in the Proceedings of the Koninklijke Akademie van Wetenschappen at Amsterdam, entitled “*On twisted curves of genus two*” (26 May 1908).

The greater part of this paper is concerned with twisted curves of genus two and of order five or six. We shall here offer a rapid survey of the results to be obtained when we apply to these curves the elementary properties of matrices, a subject upon which we have recently published a volume: *Cinq Etudes de Géométrie analytique* (Ghent, VAN GOËTHEM, 1908). We shall here occupy ourselves only with curves of order six and we shall content ourselves with observing that the quintic can be treated by analogous but more simple proceedings.

¹⁾ Cf. footnote 1 to § 7.

²⁾ With regard to the deviation from MATTHIESEN's theorem at liquid hydrogen temperatures, mentioned sub § 1, we also refer to the publications mentioned in the footnote 1 to § 7.

We have to return first to a circular sextic of which we have sketched the theory in the *Comptes-rendus de l'Académie des Sciences* of Paris (27 July 1908, pages 322—324); we shall remember briefly, whilst completing them, the immediate properties and we shall then point out how we deduce from it the theory of the most general sextic of genus two.

Let me say, by the way, that the method we make use of has a more general scope. Indeed, we see the theoretical possibility of using it for every algebraic twisted curve. For HALPHEN defines such a curve as the locus of a point the coordinates of which are algebraic functions of a same parameter t ; each of these coordinates is thus connected with t by an integer algebraic equation; it suffices to put down the conditions in order that these three equations be satisfied by a same value of t ; and it is in several ways possible to express these conditions by the disappearance of a matrix: the representation of CAYLEY by means of cone and monoid forms at bottom a solution of the problem. We have pointed out an other one in our *Cinq Études* (p. 60) and others can still be found; but most of the times the curve under consideration is found accompanied by curves of an inferior order.

1. Let us now return to the real subject of our paper.

Let

$$S_i \equiv a_i (x^2 + y^2 + z^2) + s_i \quad (i = 1, 2, 3, 4, 5, 6)$$

be in rectangular cartesian coordinates the equations of six independent spheres (the functions s_i are linear in x, y, z). The equations

$$\frac{S_1}{S_4} = \frac{S_2}{S_5} = \frac{S_3}{S_6} \quad \text{or} \quad \begin{vmatrix} S_1 & S_2 & S_3 \\ S_4 & S_5 & S_6 \end{vmatrix} = 0 \quad \dots \quad (1)$$

represent besides the imaginary circle at infinity a twisted curve γ_6 of order six, of genus two, containing six points of the imaginary circle at infinity.

We shall now and then write the equations (1) in abridged form $S_1 S_4 = 0$ and we shall suppose emphatically that the matrix $|a_1 a_4|$ is not zero, without which $x^2 + y^2 + z^2$ might cause by subtraction the denominators of the fractions (1) to disappear and the curve would be of order five of which the theory is analogous to that of γ_6 , but simpler.

The curve γ_6 is on ∞^2 cyclids $|a_1 S_1 S_4| = 0$, two of which intersect each other still according to a quadrisecant circle of γ_6 . The equations of such a circle can be written

$$\left. \begin{aligned} \Sigma \lambda_1 S_1 &\equiv \lambda_1 S_1 + \lambda_2 S_2 + \lambda_3 S_3 = 0, \\ \Sigma \lambda_1 S_4 &\equiv \lambda_1 S_4 + \lambda_2 S_5 + \lambda_3 S_6 = 0 \end{aligned} \right\} \dots \dots (2)$$

and we can easily deduce from them a theory pretty well detailed of the congruence of these quadrisecant circles of γ_6 . Thus we see that this congruence is of order one and of class three; that those circles which pass through a fixed point of γ_6 generate a cyclid having this point as a node; that those circles of which the plane passes through a fixed point generate a surface of order seven; we find the surface which is generated by those circles resting on a right line or on a curve, etc., etc. The most important result is that the planes of these circles envelop a cubic scroll Sc_3 .

Every sphere containing a quadrisecant circle of γ_6 has an equation of the form

$$\Sigma \lambda_1 (S_1 - k S_4) = 0 \dots \dots \dots (3)$$

and it contains the two points for which we have $S_1 = kS_4, S_2 = kS_5, S_3 = kS_6$. When k varies these two points describe the fundamental involution discussed by Prof. JAN DE VRIES; we simply shall call *couples*, the couples of points of this involution. The chords of *couples* are the rectilinear generatrices of the surface Sc_3 .

Among the surfaces $[a_1 S_1 S_4]$ circumscribed about γ_6 , we must distinguish the two following

$$a_1 S_1 S_4 = 0, \quad [a_4 S_1 S_4] = 0 \dots \dots \dots (4)$$

They are *circular cubics* and they determine a pencil the base of which completes itself by means of the circle at infinity and of the line

$$a_1 \quad a_4 \quad S_1 \quad S_4 \quad || = 0; \dots \dots \dots (5)$$

by subtraction of the columns this matrix is reduced to $||[a_1 a_4 s_1 s_4]$ and represents a right line q , quadrisecant of γ_6 , double line of the surface Sc_3 and meeting all the chords of the *couples*.

2. Let us write the equations of the sphere S_i in the more complete form

$$S_i \equiv a_i(x^2 + y^2 + z^2) + b_i x + c_i y + d_i z + f_i = 0,$$

let us put the matrix

$$M \equiv || a_i \ b_i \ c_i \ d_i \ f_i || \quad (i = 1, 2, 3, 4, 5, 6)$$

and let us call M_i the determinant deduced from this matrix by the omission of the row of rank i and affected by the sign $+$ or $-$ according to i being even or odd; we shall then have evidently

$$\left. \begin{aligned} \Sigma M_i a_i &= \Sigma M_i b_i = \Sigma M_i c_i = \Sigma M_i d_i = \Sigma M_i f_i = 0, \\ \Sigma M_i S_i &\equiv 0. \end{aligned} \right\} \dots \dots (6)$$

Consequently the two following equations are perfectly equivalent

$$\left. \begin{aligned} (S_1 - kS_4)(M_4 + lM_1) + (S_2 - kS_5)(M_5 + lM_2) + (S_3 - kS_6)(M_6 + lM_3) &= 0 \\ (S_1 - lS_4)(M_4 + kM_1) + (S_2 - lS_5)(M_5 + kM_2) + (S_3 - lS_6)(M_6 + kM_3) &= 0. \end{aligned} \right\} (7)$$

They represent visibly one as well as the other the sphere brought through the two *couples* defined by the parameters k and l . Each of these equations can, by putting $\Sigma M_i S_i$ instead of $M_4 S_1 + M_5 S_2 + M_6 S_3$, etc., be written in the abridged form

$$\Sigma M_i S_i + (k + l) \Sigma M_i S_i - kl \Sigma M_i S_i = 0. \quad . \quad . \quad (8)$$

For k and l variable we have a double infinity of spheres or rather a net of spheres, for they all pass through two fixed points D_1 and D_2 of γ_6 , points for which the three following expressions are annulled at the same time:

$$\Sigma M_i S_i, \quad \Sigma M_i S_i \text{ or } - \Sigma M_i S_i, \quad \Sigma M_i S_i.$$

These points D_1 and D_2 are on any sphere containing two *couples*, thus also in the plane of two *couples* of which the chords cut each other (on the quadriseccant q); so $D_1 D_2$ is the simple line of the surface Sc_3 through which pass all the bitangent planes of this surface.

We find that the line $D_1 D_2$ has as equations

$$\begin{aligned} \Sigma S_i M_i & \quad \Sigma S_i M_i & \quad \Sigma S_i M_i & = 0. \quad . \quad . \quad (9) \\ \Sigma a_i M_i & \quad \Sigma a_i M_i & \quad \Sigma a_i M_i & \end{aligned}$$

In order that it may mix up with the line q or that the surface Sc_3 may be a special cubic scroll of CAYLEY we must have the condition

$$\Delta = \begin{aligned} & \Sigma a_i M_i & \quad \Sigma a_i M_i \\ & \Sigma a_i M_i & \quad \Sigma a_i M_i \end{aligned} = 0. \quad . \quad . \quad (10)$$

The determinant Δ is the product out of the columns of the two matrices $\begin{bmatrix} a_i & a_i \end{bmatrix}$ and $\begin{bmatrix} M_i & M_i \end{bmatrix}$; its disappearance corresponds to a special case in which the curve γ_6 acquires certain exceptional, remarkable properties which cannot be mentioned here for want of space.

3. Since the curve γ_6 belongs to the base of a pencil of cubic circular surfaces and to a surface Sc_3 which is not an element of this pencil, it is found on all the cubic surfaces of a certain net. Any two of these surfaces intersect each other according to the curve γ_6 , the quadriseccant q , and a conic c_2 . This conic cuts γ_6 in six points and reciprocally every conic cutting γ_6 six times belongs to a pencil of circumscribed cubic surfaces.

The preceding allows us to write the equations of γ_6 in a new

form. Two circular cubic surfaces containing the curve have equations of the form

$$\begin{aligned} a_1 S_1 S_4 &= a_1 s_1 s_4 + (x^2 + y^2 + z^2) [a_1 s_1 a_4] = 0, \\ a_4 S_1 S_4 &= [a_4 s_1 s_4] + (x^2 + y^2 + z^2) [a_4 a_1 s_4] = 0. \end{aligned}$$

The intersection of these surfaces from which the circle at infinity will be subtracted will verify the relations

$$\begin{array}{ccc} x^2 + y^2 + z^2 & [a_1 s_1 s_4] & [a_4 s_1 s_4] \\ 1 & [a_1 a_4 s_1] & [a_1 a_4 s_4] \end{array} = 0, \dots (11)$$

which thus represent the curve γ_6 with its quadriseccant q ; the determinant of the two last columns is annulled for the scroll S_3 .

We thus find that the curve γ_6 accompanied by its quadriseccant q constitutes a special case of a curve of order seven and genus 5, annulling a matrix of three columns and two rows, one of quadratic forms, the other of linear forms, curve of order seven which we have discussed in our *Cinq Etudes* (p. 44) in giving the bibliography.

By causing the matrix (11) to be preceded by a line of constants we find the net of cubic surfaces circumscribed to γ_6 . Two of these surfaces intersect each other still according to a sexiseccant conic of γ_6 , conic of which the equations are

$$\left. \begin{aligned} \mu_1 (x^2 + y^2 + z^2) + \mu_2 [a_1 s_1 s_4] + \mu_3 [a_4 s_1 s_4] &= 0, \\ \mu_1 + \mu_2 [a_1 a_4 s_1] + \mu_3 [a_1 a_4 s_4] &= 0. \end{aligned} \right\} \dots (12)$$

The second of these equations represents the plane of the conic; we see that this plane is parallel to the line q and that every plane parallel to q contains a sexiseccant conic of γ_6 .

The equations (12) represent the congruence of the sexiseccant conics of γ_6 ; it is a *particular* case of a congruence considered by Mr. MONTESANO (*Atti Accad. Torino*, 1892); we see that it is of order one and of class one; that the planes of those conics which break up into two triseccant lines of γ_6 envelop a cylinder of class four etc.

If we let the matrix (11) be followed by a column of which the first element is an arbitrary linear form a_x and the second an arbitrary constant β , we obtain a matrix which is annulled for eight points of which six are on γ_6 and two are on the quadriseccant; they are the intersections of γ_6 and of q with the sphere

$$(x^2 + y^2 + z^2) \beta - a_x = 0.$$

If we make in this equation β and the coefficients of a_x to vary, we have all the possible spheres; on the other hand we verify

immediately that the eight points in question and any sexisecant conic of γ_6 are always on a same quadric.

In other words: every sexisecant conic of γ_6 plays a part analogous to that of the imaginary circle at infinity which is also a sexisecant conic of γ_6 .

4. This last observation suggests an other one of greater importance.

By means of a linear transformation which replaces the circle at infinity by an other conic the curve γ_6 becomes the most general twisted sextic of genus two. Really HALPHEN (*École polytechnique* 52^{ème} cah., 1882) has shown that such a sextic is the partial intersection of two cubic surfaces which have still a line and a conic in common and it is implied that this right line and this conic do not meet. So let us take the plane of the conic as face x_1 of the tetrahedron of reference and the right line as edge x_2x_3 of this tetrahedron. The equation of one of the cubic surfaces has the form

$$x_1a_x^2 = b_x^2c_x, \dots \dots \dots (13)$$

the second member being independent of x_1 ; $b_x^2 = 0$ is the cone with vertex $x_2x_3x_4$ perspective to the conic of the plane x_1 ; the line x_2x_3 belonging to the surface must annul the linear form c_x and consequently also the quadratic form a_x^2 .

For the same reasons an other cubic surface circumscribed to the considered system of lines has as equation

$$x_1a_x'^2 = b_x^2c_x', \dots \dots \dots (14)$$

where $a_x'^2$ and c_x' pass still through the line x_2x_3 .

Omitting the conic $x_1 = 0, b_x^2 = 0$, the intersection of these two surfaces annuls the matrix

$$\begin{matrix} x_1 & c_x & c_x' \\ b_x^2 & a_x^2 & a_x'^2 \end{matrix} \dots \dots \dots (15)$$

Thus every sextic of genus two forms with its quadrisecant a degenerated system of a curve of order seven and of genus five; this system annuls a matrix of three columns and two rows, one of linear forms, the other of quadratic forms where the elements of two columns are annulled for a same line.

Now it is easy to see that any such matrix leads back to an other of six quadrics having one conic in common. And really, the quadrics a_x^2 and $a_x'^2$ passing through the line c_xc_x' can be replaced by $c_xp_x + c_x'q_x$ and $c_xp_x' + c_x'q_x'$; then two determinants deduced from the matrix (15) can be written:

$$x_1(c_xp_x + c_x'q_x) - c_xb_x^2 = 0, \quad x_1(c_xp_x' + c_x'q_x') - c_x'b_x^2 = 0,$$

whence for the points which do not annul c_x and c_x' at the same time,

$$\begin{array}{ccc} c_x & x_1 q_x & b_x^2 - x_1 q'_x \\ c'_x & b_x^2 - x_1 p_x & x_1 p'_x \end{array} = 0;$$

by multiplying the terms of the first column by x_1 and by applying in any arbitrary way the addition of the rows and the columns, there is always a matrix of six quadratic forms annulling itself for the conic $x_1 = b_x^2 = 0$.

The projective theorems relating to the circular sextic γ_6 can thus be translated into properties of the most general sextic of genus two. It is superfluous to write down how these theorems run; we shall quote but one as an example; in every sextic of genus two the planes of the sexisecant conics pass through a fixed point of the quadrisecant.

5. If the intersection of the two cubic surfaces considered in the preceding (13) and (14) is completed by a line and a conic having a point in common, we have not a special case of the preceding case, in the sense of HALPHEN; but this line and this conic form a special case of a twisted cubic and the sextic is then of order three. Really in this case the equations (13) and (14) can be such that the line $x_2 x_3$ annuls $a_x^2, a'_x{}^2$ and b_x^2 without annulling c_x or c'_x and the matrix

$$\begin{array}{ccc} x_1 & c_x & c'_x \\ b_x^2 & a_x^2 & a_x'^2 \end{array}$$

has then the elements of its second row disappearing for a same line.

By this proceeding we can study the sextic of genus three; we can refine the univalent correspondence between its points and its trisecants, correspondence found by Mr. F. SCHUR (*Math. Ann.* vol. 18); we can bring back the representation of the curve to a matrix of twelve linear forms which we have studied in our *Cinq Etudes* and in the *Bulletins de l'Académie royale de Belgique* (May 1907), etc.

Ghent, Oct. 26, 1908.

Mathematics. — “On the combinatory problem of STEINER.” By Dr. J. A. BARRAU. Communicated by Prof. D. J. KORTEWEG. (Communicated in the meeting of October 31, 1908).

In its most general form this problem runs as follows:

for which values of n and in how many really different¹⁾ ways is it possible to write down a number of combinations p to p of n elements in such a way that all combinations q to q appear in it, each one time?

¹⁾ i. e. which do not pass into each other by means of substitutions of the n elements.

A geometrical way of putting the question is this:

which combinatory configurations whose points S_0 are represented by the combinations q to q of n letters, whilst the combinations p to p represent its Sp_{p-q} , possess systems of Sp_{p-q} containing all points of the C_f each one time and how many types of such systems appear in each definite case?

The first question gave rise to investigations for $= 3, q = 2$, the triple systems (KIRKMAN, REISS, NETTO, MOORE, HEFFTER, BRUNEL¹⁾); the second question is discussed by J. DE VRIES²⁾ and CARP³⁾.

Here some results are communicated for $p > 3, q > 2$. We adhere for this to the first form of the question and we call a system as is demanded there an $S(p, q), n$.

If we isolate in an $S(p, q), n$ all sets of p having in common a certain arbitrarily chosen letter, and if we omit that letter from it, an $S(p-1, q-1), n-1$ is generated; repetition of the operation gives rise to an $S(p-2, q-2), n-2$ and so on; the possibility of an $S(p, q)$ presupposes thus that of a series of systems of lower rank⁴⁾, which series can be broken off at

$$S(p - q + 2, 2), n - q + 2$$

Inversely all imaginable systems are acquired by completion of systems commencing with $q = 2$.

So we can expect:

$$\begin{array}{l} \text{out of } S(3, 2), n = 7 : S(4, 3), n = 8 \quad . \quad . \quad . \quad A \\ \text{out of } S(3, 2), n = 9 : S(4, 3), n = 10 \quad . \quad . \quad . \quad B \\ \qquad \qquad \qquad \qquad \qquad S(5, 4), n = 11 \quad . \quad . \quad . \quad C \\ \qquad \qquad \qquad \qquad \qquad S(6, 5), n = 12 \quad . \quad . \quad . \quad D \end{array}$$

etc. We will show that the four systems mentioned exist each of them in one type.

¹⁾ Cambridge and Dublin Math. Journal II, 1847; Journal f. d. r. u. a. Mathem. 56, 1859; Mathem. Annalen 42, 1893; 43, 1893; 49, 1897; 50, 1898; Association française, Congrès de Bordeaux 1895; Journal de Liouville (5) VII, 1901.

²⁾ Versl. en Meded. Kon. Akad. v. Wet. 3rd series, VI, p. 13, 1889; Mathem. Annalen 34, 35, 1889, '90.

³⁾ Dissertation, Utrecht 1902, p. 38.

⁴⁾ For each system of the series the condition must be satisfied: $\binom{n}{q}$ divisible by $\binom{p}{q}$. Thus there will be no $S(6, 4), n = 15$, although $\binom{15}{4}$ is divisible by $\binom{6}{4}$, on account of the impossibility of an $S(5, 3) n = 14$: $\binom{14}{3}$ is not divisible by $\binom{5}{3}$.

A. An $S(4, 3)$, $n = 8$ consists of $\binom{8}{3} : \binom{4}{3} = 14$ quadruplets, so it is a schematic Cf. $(8_7, 14_4)$. If we add to the triplets of an $S(3, 2)$, $n = 7$, that is of a Cf. (7_2) a new letter, and if out of the quadruplets thus formed we choose one, then in the completion with seven new quadruplets sought for the pairs of the selected triplets must appear still twice: so a new quadruplet remains, complementary to the one selected.

This holds for each quadruplet; the whole completion is thus complementary and only possible in one way ¹⁾.

B. If in an $S(4, 3)$, $n = 10$, that is a Cf. $(10_{12}, 30_4)$, we choose an arbitrary quadruplet 1 2 3 4, each pair of these letters appears in three more quadruplets: so there are 18 more such quadruplets. Then each single letter appears two times more, completed with triplets out of 5, 6, 7, 8, 9, 0, which triplets form thus together a Cf. $(6_4, 8_3)$. Of the whole system only three quadruplets out of 5, 6, 7, 8, 9, 0 remain, which in pairs may have at most only two letters in common. Such systems of three exist however only in one type ²⁾, as:

$$5\ 6\ 7\ 8 \quad ; \quad 5\ 6\ 9\ 0 \quad ; \quad 7\ 8\ 9\ 0,$$

with which the system to be formed must commence. The eight triplets of letters missing here form of necessity the Cf. $(6_4, 8_3)$, which breaks up only in *one* way into four pairs completing each other. If we complete these pairs respectively with 1, 2, 3 and 4 (in which order is irrelevant) the following quadruplets are formed:

$$\begin{array}{cccc} 1\ 5\ 7\ 9 & ; & 2\ 5\ 7\ 0 & ; & 3\ 5\ 8\ 9 & ; & 4\ 5\ 8\ 0 \\ 1\ 6\ 8\ 0 & ; & 2\ 6\ 8\ 9 & ; & 3\ 6\ 7\ 0 & ; & 4\ 6\ 7\ 9. \end{array}$$

The entire further completion is now determined and *must* run as follows:

$$\begin{array}{cccc} 1\ 4\ 5\ 6 & ; & 1\ 2\ 5\ 8 & ; & 2\ 3\ 7\ 9 & ; \\ 2\ 3\ 5\ 6 & ; & 1\ 2\ 6\ 7 & ; & 2\ 3\ 8\ 0 & ; \\ 1\ 3\ 7\ 8 & ; & 1\ 3\ 5\ 0 & ; & 2\ 4\ 5\ 9 & ; \\ 2\ 4\ 7\ 8 & ; & 1\ 3\ 6\ 9 & ; & 2\ 4\ 6\ 0 & ; \\ 1\ 2\ 9\ 0 & ; & 1\ 4\ 7\ 0 & ; & 3\ 4\ 5\ 7 & ; \\ 3\ 4\ 9\ 0 & ; & 1\ 4\ 8\ 9 & ; & 3\ 4\ 6\ 8 & . \end{array}$$

Now that with this the existence of only *one* type is assumed, we can give it a simpler form; we shall do this in two ways.

¹⁾ The scheme $(8_7, 14_4)$ indicates in the measure-polytope B_8 the vertices, forming with point zero and its opposite vertex together a cross-polytope C_8 (*Nieuw Archief v. Wisk.* 2nd Series, VII, p. 255).

²⁾ The complementary type of a division of six elements into three pairs

We in the first place remember that the $S(3, 2)$, $n = 9$ deduced from $S(4, 3)$, $n = 10$ is *regular commutative* (MOORE), i. e. that its group possesses a regular commutative subgroup of the type :

1	2	3	4	5	6	7	8	9
2	3	1	5	6	4	8	9	7
3	1	2	6	4	5	9	7	8
4	5	6	7	8	9	1	2	3
5	6	4	8	9	7	2	3	1
6	4	5	9	7	8	3	1	2
7	8	9	1	2	3	4	5	6
8	9	7	2	3	1	5	6	4
9	7	8	3	1	2	6	4	5

Indeed, an $S(3, 2)$, $n = 9$ appears if we submit the triplets

1 2 3 ; 1 4 7 ; 1 5 9 ; 1 6 8

to all the substitutions of this group.

If we now add to each of these twelve triplets a zero and if we submit the quadruplets

1 2 4 5 and 1 2 6 9

to the substitutions of the group, then the $12 + 18 = 30$ quadruplets of the $S(4, 3)$, $n = 10$ are formed.

Secondly we observe, that the system is cyclic and appears among others by submitting the quadruplets

1 2 3 7 ; 1 2 4 5 ; 1 3 5 8

to the cycle (1 2 3 4 5 6 7 8 9 0).

C. If we choose out of an $S(5, 4)$, $n = 11$, that is a Cf. (11₃₀, 66₄), a quintuple 1 2 3 4 5, then all triplets of it must appear still three times, all pairs moreover still two times, the single letters afterwards three times, with which the $10 \times 3 + 10 \times 2 + 5 \times 3 = 65$ remaining quintuplets of the system are exhausted. The single letters are completed with quadruplets out of 6, 7, 8, 9, 0, *a*, which may have at most three letters in common and which form together a Cf. (6₁₀, 15₄), consisting of five (6₃, 3₄) as appeared in *B*. Of this but *one* type exists ¹⁾, so that e. g. the $S(5, 4)$ commences with:

1	8	9	0	<i>a</i>		2	7	9	0	<i>a</i>		3	7	8	0	<i>a</i>		4	7	8	9	<i>a</i>		5	7	8	9	0
1	6	7	0	<i>a</i>		2	6	8	9	<i>a</i>		3	6	8	9	0		4	6	8	0	<i>a</i>		5	6	9	0	<i>a</i>
1	6	7	8	9		2	6	7	8	0		3	6	7	9	<i>a</i>		4	6	7	9	0		5	6	7	8	<i>a</i>

¹⁾ Deduced from the well-known system of five three-divisions of six elements of **SERRET**.

The further constitution is now determined and must run as follows :

1 2 6 9 0	1 4 6 9 a	2 3 6 0 a	2 5 6 7 9	3 5 6 7 0
1 2 7 8 a	1 4 7 8 0	2 3 7 8 9	2 5 8 0 a	3 5 8 9 a
1 3 6 8 a	1 5 6 8 0	2 4 6 7 a	3 4 6 7 8	4 5 6 8 9
1 3 7 9 0	1 5 7 9 a	2 4 8 9 0	3 4 9 0 a	4 5 7 0 a
1 2 3 6 7	1 2 5 6 a	1 3 5 6 9	2 3 4 6 9	2 4 5 6 0
1 2 3 8 0	1 2 5 7 0	1 3 5 7 8	2 3 4 7 0	2 4 5 7 8
1 2 3 9 a	1 2 5 8 9	1 3 5 0 a	2 3 4 8 a	2 4 5 9 a
1 2 4 6 8	1 3 4 6 0	1 4 5 6 7	2 3 5 6 8	3 4 5 6 a
1 2 4 7 9	1 3 4 7 a	1 4 5 8 a	2 3 5 7 a	3 4 5 7 9
1 2 4 0 a	1 3 4 8 9	1 4 5 9 0	2 3 5 9 0	3 4 5 8 0

A simple form of the system¹⁾ is obtained by submitting the quintuplets

$$1\ 2\ 3\ 4\ 0;\quad 1\ 2\ 3\ 5\ 8;\quad 1\ 2\ 3\ 6\ 7;$$

$$1\ 2\ 4\ 5\ 9;\quad 1\ 2\ 4\ 6\ 8;\quad 1\ 2\ 5\ 7\ 0$$

to the cycle :

$$(1\ 2\ 3\ 4\ 5\ 6\ 7\ 8\ 9\ 0\ a).$$

D. By a reasoning analogous to that in section A is evident that $S(6,5)$, $n = 12$, that is a Cf. $(12_{6a}, 132_a)$ must appear by complementary completion of $S(5,4)$, $n = 11$, so it appears only in one type.

In general out of each

$$S(p = q + 1, q),\ n = 2q + 3$$

is formed by complementary completion an

$$S(p = q + 2, q + 1),\ n = 2q + 4.$$

Passing to systems $S(p, q = 2)$, n for arbitrary $p^2)$, we observe that for their existence is necessary at least :

$$\frac{n(n-1)}{1.2}\ \text{divisible by}\ \frac{p(p-1)}{1.2},$$

and

$$n-1\ \text{divisible by}\ p-1,$$

which conditions are fulfilled only by the two series of numbers

$$\begin{array}{l} I \\ II \end{array} \quad \left. \begin{array}{l} n = p(p-1) \cdot x + 1 \\ n = p(p-1) \cdot x + p \end{array} \right\} x = 0, 1, 2, \dots$$

¹⁾ A $S(5,4)$, $n = 11$ was given by LEA (*Educ. Times IX*), the method in which this was generated is unknown to me, as this publication was not attainable for me; however, the system must be of the same type. We remark moreover, that to prove this, it is not sufficient to assert that all remainders have a fixed type, comp. MARTINETTI (*Annali di Matem.* (2) XV). The same holds for A, B and D.

²⁾ These $S(p,2)$ are to be distinguished from the systems of BRUNEL, in which each set of p is regarded as containing only the p pairs of elements succeeding each other (*Proc. Verb. Soc. de Bordeaux*, 1895/96, p. 58 and 1898/99, p. 59, 71).

The term $x = 0$ has no significance in I ; in II it indicates that when writing all $n = p$ letters we have written at the same time all pairs of those letters. This system $II, x = 0$ will be of service in what follows.

We shall now give a more extensive form to the *multiplication-theorem* of NETTO (l.c. § 3) which becomes :

Out of an $S(p,2)_{n_1}$ and an $S(p,2)_{n_2}$ an $S(p,2)_{n_1 n_2}$ can be deduced, if one disposes of a system of $p(p-1)$ permutations of p elements, in which a couple of elements never occupies the same place.

For, if the elements of the two systems are resp. $a_k (k = 1, 2, \dots, n_1)$ and $b_l (l = 1, 2, \dots, n_2)$ we can then designate $n_1 n_2$ new elements by $c_{k,l}$. Of these elements we form *three* kinds of p sets of p , namely:

1st. out of *each* set of p $a_1 a_2 \dots a_p$ new p -sets:

$$c_{1,l}, c_{2,l}, \dots, c_{p,l} \quad (l = 1, 2, \dots, n_2);$$

2nd. out of *each* set of p $b_1 b_2 \dots b_p$ new p -sets:

$$c_{k,1}, c_{k,2}, \dots, c_{k,p} \quad (k = 1, 2, \dots, n_1);$$

3rd. out of *each* set of p $a_1 a_2 \dots a_p$, combined with *each* set of p $b_1 b_2 \dots b_p$ new p -sets:

$c_{1,l_1}, c_{2,l_2}, \dots, c_{p,l_p}$, where l_1, \dots, l_p are every time the same as the indices $1, \dots, p$ of the set of p of b , yet differ $p-1$ times in order of succession according to the $p-1$ permutations of the system of permutations supposed as disposable.

It is clear that in this way a couple of the new elements can never appear more than once whilst the number of formed sets of p amounts to :

$$n_2 \frac{n_1(n_1-1)}{p(p-1)} + n_1 \frac{n_2(n_2-1)}{p(p-1)} + p(p-1) \frac{n_1(n_1-1)}{p(p-1)} \cdot \frac{n_2(n_2-1)}{p(p-1)} = \frac{n_1 n_2 (n_1 n_2 - 1)}{p(p-1)},$$

so that really an $S(p,2)_{n_1 n_2}$ is formed.

Now we dispose of such a permutation-system, when :

1) $p = 4$: the twelve even permutations;

2) p *prime*, the system then consists of:

$$\begin{aligned} & (1, 2, 3, 4 \dots p)_{cyc.} \\ & (1, 3, 5, 7 \dots p-1)_{cyc.} \\ & (1, 4, 7, 10 \dots)_{cyc.} \\ & \dots \dots \dots \\ & (1, p, p-1, p-2 \dots 2)_{cyc.}^1. \end{aligned}$$

¹⁾ Comp. e.g. BRUNEL, *Proc. Verb. Soc. de Bordeaux* 1894/95, p. 56, or AHRENS, *Mathematische Unterhaltungen*, p. 272: "Promenaden von n^2 Personen zu je n ". It is not decided whether also other values of p allow a solution.

(For $p = 3$ the system just contains the total group and so the theorem of NETTO reappears).

So we have:

The possibility of the multiplication is assured for $p = 4$ or prime.

Now by taking as factors $n_1 = n_2 = p$, so term $II, x = 0$, we obtain :

For $p = 4$ or prime the existence of $S(p, 2), n = p^2$ is assured.

Such a system, term $II, x = 1$ is, regarded as Cf.-scheme, a Cf. $\{p^2_{p+1}, p(p+1)_p\}$; its p -sets can be divided into $(p + 1)$ principal groups of p , each of which contains all the p^2 elements.

We can now give in a more extensive form an other theorem of NETTO (i.e. § 2), which becomes here:

Out of an $S(p, 2), n$ an $S(p, 2), (p-1)n + 1$ can be formed if we have at our disposal a scheme of $(p-1)^2$ sets of p out of $p(p-1)$ elements, having mutually not more than one element in common, which elements must be able to break up into p principal groups of $(p-1)$.

For, we can add to the elements $a_{1,1}, a_{1,2} \dots a_{1,n}$ of the given system $(p-2)$ series of new ones:

$$\begin{matrix} a_{2,1} & , & a_{2,2} & , & \dots & , & a_{2,n} \\ \dots & & \dots & & \dots & & \dots \\ a_{p-1,1} & , & a_{p-1,2} & , & \dots & , & a_{p-1,n} \end{matrix}$$

and moreover a last element a_0 .

For each set of p of the given system we must now form out of the $p(p-1)$ elements with the same second indices a scheme as the one indicated in the theorem, taking care that always the $(p-1)$ elements with equal second index form a principal group. Finally we must add to each principal group the element a_0 , by which also these principal groups are completed to p . It is clear that the sets of p formed in this way can have two by two at most but *one* element in common, while their number amounts to:

$$(p-1)^2 \cdot \frac{n(n-1)}{p(p-1)} + n = \frac{\{(p-1)n+1\}\{(p-1)n\}}{p(p-1)},$$

so that an $S(p, 2), (p-1)n + 1$ is formed.

The possibility of the method now depends on the presence of a scheme:

$$\{p(p-1)_{p-1}, (p-1)^2_p\}$$

or, replacing p by $p-1$, of

$$\{p(p+1)_p, p^2_{p+1}\},$$

but that is just the notation of the above-mentioned $S(p, 2), n = p^2$,

if but in the diagram we exchange rows and columns. It satisfies, moreover the further conditions; so we have:

The deduction of an $S(p, 2)$, $(p-1)n + 1$ out of an $S(p, 2)$, n is assured, when $p = 5$ or a prime number $+ 1$.

If we apply this to $n = p$, we find:

The existence of $S(p, 2)$, $n = p(p-1) + 1$ is assured for $p = 5$ or a prime number $+ 1$.

These systems form the term I, $x = 1$; as Cf.-schemes they are Cf. $\{p(p-1) + 1_p\}$.

It is clear that their remainders to *one* element again become $S(p-1, 2)$, $n = (p-1)^2$, that is term II, $x = 1$ out of the series $p-1$.

In cyclic form we find:

$$n = 13, \quad p = 4 : (1, 2, \dots 5, \dots 7) \text{ cyc.}$$

$$n = 21, \quad p = 5 : (1, 2, \dots 5, \dots 15, \dots 17 \dots) \text{ cyc.}$$

$$n = 31, \quad p = 6 : (1, 2, \dots 5, \dots 7 \dots 14, \dots 22 \dots) \text{ cyc. } ^1)$$

We finally pass on to the generation of an $S(4, 2)$, $n=25$.

As Cf. the system is a Cf. $(25_8, 50_4)$, the remainder to each quadruplet is a Cf. (21_4) . The latter must have the property that the non-united elements may be united to triplets, so that out of it arises a Cf. $(21_4, 28_8)$ which breaks up into four principal-7-sides²⁾. By imagining the seven lines of such a 7-side to be every time convergent to *one* point and the four points of convergence to be collinear, the desired Cf. $(25_8, 50_4)$ is formed.

We obtain a solution by submitting

$$1, \dots 3, \dots 9, \dots 12;$$

$$1, \dots 8, \dots 15 \quad , \text{ (completed by 22);}$$

$$1, \dots 2, \dots 6 \quad , \text{ (in turns completed by 23, 24 and 25);}$$

to the cycle

$$(1, 2, 3, \dots 21)$$

and by finally adding:

$$22, 23, 24, 25.$$

In like manner we shall find that in general an

$$S(p, 2), \quad n = 2p(p-1) + 1,$$

that is a Cf. $\{2p(p-1) + 1_{2p}, 4p(p-1) + 2_p\}$,

¹⁾ Comp. E. MALO, (*Interm. des Mathém.* XVI, p. 63). The $2p$ cycles given there for each p are mutually identical and so they furnish every time but one type.

²⁾ Comp. a former paper in these Proceedings (p. 290). In the mean time I have found that the result given there, in as far as it concerns $n = 13$ is obtained in about the same way by BRUNEL (*Journal de Liouville*, 1901), and already in 1899 by DE PASQUALE, *Rendic. R. Inst. Lombardo* (2) 32, p. 213.

will consist of a

$$\text{Cf. } \{(2p - 1)(p - 1)_p\},$$

whose missing pairs of elements can be united to sets of $(p-1)$, so that a

$$\text{Cf. } \{2p(p - 1)_p, p(2p - 1)_{p-1}\}$$

is formed which breaks up into p principal- $(2p - 1)$ -sides.

As in the series $p=4$, just as for $p=3$, the two extensions of the theorems of NETTO can be applied, we can form, in the first set of hundred, systems $S(4, 2)$ for:

$$n = 13, 25, 49; 4, 16, 40, 52, 64, 76, 100.$$

The still missing values are:

$$n = 37, 61, 73, 85, 97; 28, 88,$$

of which 85 might be acquired by 28.

Physics. — “*Remarks on the Leyden observations of the Zeeman-Effect at low temperatures.*” By W. VOIGT. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the Meeting of October 31, 1908).

The observations of KAMERLINGH ONNES and JEAN BEQUEREL¹⁾ on the ZEEMAN-Effect at exceedingly low temperatures have led to some surprising results, among which are two, very interesting from the theoretical standpoint. These I will try to throw light upon in the following.

I. It has been found, when the observation was made along the optic axis of an uniaxial crystal (where such a body acts as if isotropic) a longitudinal magnetic field being used, that the components of the ZEEMAN-doublet have different intensities. The component on the side of the shorter wave-length had generally (though not always) the greater intensity.

This result seems to show, that in the crystal one sense of rotation is preferred to the other. Therefore it might be interesting, to consider firstly the effect of a magnetic field on a naturally active crystal. I may at this point remark that, contrary to what should be expected, the effects of the natural activity and of the magnetic field do not superpose each other, but rather singular combined effects appear in the neighbourhood of an absorption band.

¹⁾ J. BEQUEREL and KAMERLINGH ONNES. These Proceedings February 29th 1908.

The following notation will be made use of:

A, B, C components of magnetic force.

X, Y, Z „ „ electric „

$\mathfrak{A}, \mathfrak{B}, \mathfrak{C}$ „ „ magnetic polarization.

$\mathfrak{X}, \mathfrak{Y}, \mathfrak{Z}$ „ „ electric „

$\mathfrak{r}_h, \mathfrak{v}_h, \mathfrak{i}_h$ „ „ electric partial polarizations.

$a_h, b_h, c_h, \sigma_h, \epsilon_h$ parameters.

P external magnetic force, supposed // Z .

v velocity of light in vacuum.

Then the equations of the theory based on the suppositions I have made for an isotropic active body become:

$$\mathfrak{A}' = v \left(\frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y} \right), \dots \dots \dots (1)$$

$$\mathfrak{X}' = v \left(\frac{\partial C}{\partial y} - \frac{\partial B}{\partial z} \right), \dots \dots \dots (2)$$

$$\mathfrak{r}_h + a_h \mathfrak{r}'_h + b_h \mathfrak{r}''_h + c_h P \mathfrak{v}'_h = \epsilon_h X - \sigma_h A', \dots \dots \dots (3)$$

$$\mathfrak{X} = X + \sum \mathfrak{r}_h, \dots \dots \dots (4)$$

$$\mathfrak{A} = A + \sum \sigma_h \mathfrak{r}'_h / \epsilon_h, \dots \dots \dots (5)$$

By a simple calculation we obtain for the so-called complex refractive index n in the direction of the magnetic field the value

$$n = \sqrt{(1 + E)(1 + \Theta)} \pm \Delta, \dots \dots \dots (6)$$

where

$$E = \sum \frac{\epsilon_h}{p_h \pm c_h P v}, \quad \Theta = v^2 \sum \frac{\sigma_h^2}{\epsilon_h (p_h \pm c_h P v)},$$

$$\Delta = v \sum \frac{\sigma_h}{p_h \pm c_h P v};$$

$v =$ frequency,

$$p_h = 1 + i v a_h - v^2 b_h.$$

The double sign \pm corresponds to the two waves of circular vibrations and of opposite sense of rotation propagated parallel to the field.

The complex index of refraction n is connected with the real index n and with the absorption index z by the formula $n = n(1 - iz)$. The constants σ_h and c_h measure the natural and the magnetic activity of the crystal. It is seen that even if these two effects are small in general, in the neighbourhood of an absorptionband, where p_h is of the same order as $c_h P v$, they do not superpose at all.

If the natural activity vanishes, then also Θ and Δ vanish, and we have

$$n^2 = 1 + E,$$

which contains the theory of the longitudinal ZEE MAN effect.

Among the terms arising from the natural activity that of most interest is $\pm \Delta$, which is generally much larger than Θ . This term which has opposite signs for the $+$ and the $-$ rotating waves, but which reaches its maximum at the same place as E , expresses a dissymmetry of the ZEE MAN doublet somewhat similar to that obtained in the experiments of ONNES and BECQUEREL. In order that this dissymmetry should have an appreciable magnitude it is only necessary that $v\sigma_h$ is commensurable with ϵ_h . Experience has shown that at the absorption bands of the crystals under consideration, ϵ_h is very small and so no difficulty is in the way.

Notwithstanding there is lack of agreement between the above formula and observation in two quite different directions. In the first case the observers did not notice any natural activity in the crystals they used, and from the symmetry of these crystals such was not to be expected, except in the case, that at low temperatures the constitution of the molecules changes. On the other hand the observed behaviour by a reversed magnetic field is not in agreement with the above formula.

Both objections disappear if in the formulae (3) we substitute for the terms $\sigma_h A'$, $\sigma_h B'$, $\sigma_h C'$ on the right hand side the terms O , $\sigma_h P A'$, $\sigma_h P B'$ and in the formulae (5) for the right hand terms resp. A , $B + P \sum \sigma_h y_h' / \epsilon_h$, $C + P \sum \sigma_h z_h' / \epsilon_h$. Such a series of terms corresponds exactly to the symmetry of the magnetic field and leads to the same formula (6) for n as that given above; only we have $P\sigma_h$ in place of σ_h . By this step both the above mentioned difficulties are removed; however the substitution leads from the sound basis of experience into the region of hypothesis. Observation shows that σ_h increases as the temperature diminishes.

II. In some crystals of rhombic symmetry it has appeared that in each of the three chief spectra certain absorption lines correspond to nearly the same wave length. If we observe in the direction of an axis of symmetry each of these lines is seen broken up into a doublet when the magnetic field is excited. In the present special case of equal wave length of the lines the distance of the doublet components is the same in some cases, in other cases differs. If we let the axes X , Y , Z , be parallel to the axes of the crystal and call R the direction of magnetic force, ω the direction of propagation of the ray, σ the direction of vibration, then the following table gives the result of observation:

$$\begin{array}{l}
 R//X, \omega//X \begin{cases} \sigma//Y & a_1 \\ \sigma//Z & a_1 \end{cases} \\
 \omega//Y \begin{cases} \sigma//Z & a_1 \\ \sigma//X & a'_1 \end{cases} \\
 \omega//Z \begin{cases} \sigma//X & a'_1 \\ \sigma//Y & a_1 \end{cases} \\
 R//Y, \omega//Y \begin{cases} \sigma//Y & a'_2 \\ \sigma//Z & a_2 \end{cases} \\
 \omega//Y \begin{cases} \sigma//Z & a_2 \\ \sigma//X & a_2 \end{cases} \\
 \omega//Z \begin{cases} \sigma//X & a_2 \\ \sigma//Y & a'_2 \end{cases} \\
 R//Z, \omega//X \begin{cases} \sigma//Y & a_3 \\ \sigma//Z & a'_3 \end{cases} \\
 \omega//Y \begin{cases} \sigma//Z & a'_3 \\ \sigma//X & a_3 \end{cases} \\
 \omega//Z \begin{cases} \sigma//X & a_3 \\ \sigma//Y & a_3 \end{cases}
 \end{array}$$

The theory I have developed¹⁾ makes the laws of the phenomena under consideration depend on 4×3 parameters p_h, \bar{p}_h, g_h, f_h .

p_h and \bar{p}_h ($h = 1, 2, 3$) are determined by the quasi elastic and damping forces acting on the electron in the crystal, when no magnetic field is excited. g_h ($h = 1, 2, 3$) measure the direct action of the magnetic field on the electron parallel to the axes X, Y, Z ; f_h ($h = 1, 2, 3$) determine certain couplings experienced by the electron parallel to these axes.

If we put

$$\begin{aligned}
 N_1 &= p_1 \bar{p}_1 - f_1^2 v^2, & N_{23} &= p_2 p_3 - g_1^2 v^2, \\
 N_2 &= p_2 \bar{p}_2 - f_2^2 v^2, & N_{31} &= p_3 p_1 - g_2^2 v^2, \\
 N_3 &= p_3 \bar{p}_3 - f_3^2 v^2, & N_{12} &= p_1 p_2 - g_3^2 v^2,
 \end{aligned}$$

where as before v represents the frequency, generally the magnetic effect on an absorption line in the above mentioned cases is given by the following functions:

¹⁾ W. VOIGT. Gött. Nachr. 28 Juli 1906; Magnetoptik und Electrooptik. Leipzig 1908, p. 235 u. f.

$$\begin{array}{l}
R//X, \omega//X \begin{cases} \sigma//Y & p_2/N_{23} \\ \sigma//Z & p_3/N_{23} \end{cases} \\
\omega//Y \begin{cases} \sigma//Z & p_3/N_{23} \\ \sigma//X & (p_1 + \bar{p}_1)/N_1 \end{cases} \\
\omega//Z \begin{cases} \sigma//X & (p_1 + \bar{p}_1)/N_1 \\ \sigma//Y & p_2/N_{23} \end{cases} \\
R//Y, \omega//X \begin{cases} \sigma//Y & (p_2 + \bar{p}_2)/N_2 \\ \sigma//Z & p_3/N_{31} \end{cases} \\
\omega//Y \begin{cases} \sigma//Z & p_3/N_{31} \\ \sigma//X & p_1/N_{31} \end{cases} \\
\omega//Z \begin{cases} \sigma//X & p_1/N_{31} \\ \sigma//Y & (p_2 + \bar{p}_2)/N_2 \end{cases} \\
R//Z, \omega//X \begin{cases} \sigma//Y & p_2/N_{12} \\ \sigma//Z & (p_3 + \bar{p}_3)/N_3 \end{cases} \\
\omega//Y \begin{cases} \sigma//Z & (p_3 + \bar{p}_3)/N_3 \\ \sigma//X & p_1/N_{12} \end{cases} \\
\omega//Z \begin{cases} \sigma//X & p_1/N_{12} \\ \sigma//Y & p_2/N_{13} \end{cases}
\end{array}$$

Supposing now the absorption lines to have the same *positions* in the three chief spectra, then the *real* parts of p_1, p_2, p_3 and also of $\bar{p}_1, \bar{p}_2, \bar{p}_3$ are equal; supposing the *intensities* of the absorption lines to be equal, then the *imaginary* parts are the same. If on the other hand g_1, g_2, g_3 and f_1, f_2, f_3 retain different values from each other, then also N_1, N_2, N_3 and N_{23}, N_{31}, N_{12} have different values from each other. In this case the system of distances between the doublet components obtained from theory agrees exactly with that observed. If the three absorptions are slightly different from each other, then the theoretical distances show small deviations from the mentioned law, which however will scarcely be within the range of perception.

What is interesting in the observations is that if we assume $g_1 = g_2 = g_3$, and therefore $N_{23} = N_{31} = N_{12}$ then theory is not in agreement with experience.

The parameters g_h give the direct influence of the external magnetic field on the vibrating electron. This influence appears then to be different when the field acts along the X -, the Y -, the Z -axis of the crystal. This result seems to me to verify the view I have deduced from other considerations, that the magnetic field inside the molecule, where an electron is in motion, can be very different from that in outside space. Reasoning in this way it is quite natural to imagine

that the field inside a molecule of a *crystal* gains different intensities if an external field of constant intensity acts successively parallel to the axes of the crystal.

It is true that in my former publications I have put $g_1 = g_2 = g_3$, because at that time there was no necessity to introduce more complicated suppositions. But the abovementioned observations show that generally g_1 is different from g_2 and g_3 .

If we do not accept this difference between the inner and outer field, then we must fall back on the very complicated assumptions of BECQUEREL and ONNES, that the apparent, probably electromagnetic mass of the electron is different parallel to the three axes of the crystal, and that the quasielastic forces in these directions are proportional to these masses. This would lead to the hypothesis of an immense number of different kinds of electrons, say of ellipsoidal form, which during their vibration remain parallel to themselves. The authors do not set forth how the law of the quasielastic forces would be explained. As opposed to the difficulties of this hypothesis I maintain that the above assumption of differences between the inside and outside magnetic fields is much simpler.

III. I should like to mention a general consideration arising from the preceding. It seems to me that by the irresponsible introduction of electrons which have forms masses and signs different from each other, we should lose what has been up to the present one of the chief advantages which characterise the electrontheory; the simplicity of the fundamental conception, and thus make the whole hypothesis of less value. We would have to be content with this depreciated value of the hypothesis, if we were compelled by undeniable results of experience to do so. But up to the present I cannot recognise any such evidence.

The chief objection of J. BECQUEREL to the hypothesis of inner-molecular magnetic fields lies in the fact that the ZEEMAN-effect is notably independent of temperature. But as we do not know anything definite about the cause of the inner field, it appears to me, that one cannot assert anything about the sensibility to temperature with certainty.

In this place I shall mention a consideration which seems to me to carry some weight against the precipitate assumption especially of *positive* electrons.

We learn from the theory of light that in bodies electrons oscillate about positions of equilibrium. Further the electron-theory permits only of forces of electromagnetic nature: the quasielastic forces

which bind the electrons to their equilibrium positions must therefore also be of electromagnetic nature. Thus here the only force to be considered, is electrostatic, we know from the theory of potential that an electrostatic field permits of a point-charge moving about a stable position of rest *only inside of a charge of opposite sign distributed over space*. Thus the assumption of *negative electrons* made up to the present time leads to the conception of *positive* electric charges distributed over a definite space. These two hypotheses contain no contradiction.

The assumption of *positive electrons* (of parallel properties to those of the negative) compels then to the conception of *negative* charges extended through space, and thus, as it seems to me, leads to the nullification of the whole theory. For of what use is an atomical conception of electricity which cannot be subsequently worked out?

Geophysics. — “*On Frequencies of the mean daily cloudiness at Batavia.*” By Dr. J. P. VAN DER STOK.

1. Since 1880 hourly observations of the cloudiness of the sky have been published by the Observatory at Batavia; if the daily means calculated from these records are arranged in groups, a frequency-table (Table I) is obtained which enables us to form a clear idea of the way in which the climate is affected by this highly important climatological factor.

From this Table it appears that, whilst northerly climates are characterized by a great number of cases in which the sky is entirely overcast or quite free from clouds (principally in April and September), these extreme values rarely occur at Batavia.

Only once in 26 years or in 9500 cases a serene sky lasting during 24 hours has been recorded and, taken over the whole year, the number of days during which the sky was entirely covered only amount to 1.4% and, even in full West-Monsoon, to hardly more than 4%.

Furthermore Table I exhibits the fact that, notwithstanding the great number of records, irregularities still occur to a considerable extent and the sums taken over the whole year clearly demonstrate that extreme care must be taken in adding together frequency-series of different kinds, which may lead to irregularities of the most peculiar description in the curve of distribution; and these irregularities are by no means eliminated by a greater number of data.

In order to eliminate these irregularities three natural groups have

TABLE I. Frequencies of the mean daily cloudiness as recorded at Batavia 1880—1905.

Cloud- iness	Jan.	Febr.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Total
0	—	—	—	—	—	—	—	1	—	—	—	—	1
0.5	—	—	—	—	3	10	4	4	2	2	—	—	25
1	1	—	1	2	10	11	18	19	9	9	1	—	81
1.5	2	2	2	6	10	26	39	33	21	14	4	—	164
2	5	4	1	7	36	39	52	59	37	31	9	4	284
2.5	2	7	13	25	34	52	52	75	49	36	13	4	362
3	7	7	15	35	53	52	69	84	69	44	21	5	461
3.5	5	10	30	49	70	54	78	85	88	52	30	13	564
4	9	10	33	45	70	66	71	76	89	58	33	24	584
4.5	29	24	40	59	80	68	62	74	78	84	37	31	666
5	30	23	39	64	80	55	80	58	57	63	48	33	650
5.5	39	25	70	76	60	58	56	42	62	60	62	53	663
6	51	34	73	79	58	49	46	52	38	58	62	74	674
6.5	68	69	68	88	62	44	45	32	47	60	79	53	715
7	61	77	93	67	43	43	29	42	38	56	64	64	677
7.5	78	86	84	50	50	45	24	33	33	56	76	93	708
8	100	81	77	51	39	42	23	12	19	31	78	102	655
8.5	101	90	66	36	24	33	28	13	16	40	62	94	603
9	90	94	51	29	10	16	18	7	21	32	52	67	487
9.5	93	66	39	10	8	14	6	3	6	14	38	62	359
10	35	25	41	2	1	3	6	2	1	6	11	30	133
Total	806	734	806	780	806	780	806	806	780	806	780	806	9496

been formed as shown in Table II; in these series irregularities still occur, but by far the greater part have disappeared and they furnish good material for the application and the testing of frequency-formulae.

For this purpose two alterations have to be made: in the first place the scale value has to be altered so that the extreme limits are denoted, not by 0 and 10, but by ± 1 , and consequently the origin of coordinates must be chosen in the middle between the limits;

TABLE II. Frequencies of the mean daily cloudiness, Batavia, 1880—1905.

Cloud-ness	I East Monsoon	II Trans-ition	III West-Monsoon	I East Monsoon	II Trans-ition	III West-Monsoon	New scale values
0	4	—	—	—	—	—	-1.0
0.5	23	2	—	6	4	—	-0.9
1	67	13	4	17	4	—	-0.8
1.5	134	26	4	34	8	2	-0.7
2	223	48	13	56	15	6	-0.6
2.5	262	87	13	66	27	6	-0.5
3	327	145	49	82	36	8	-0.4
3.5	375	161	28	94	51	12	-0.3
4	372	169	43	93	53	18	-0.2
4.5	362	220	84	91	69	36	-0.1
5	330	244	86	83	68	37	0.0
5.5	278	268	117	70	84	50	0.1
6	243	272	159	61	86	68	0.2
6.5	230	295	190	58	93	81	0.3
7	195	280	202	49	88	86	0.4
7.5	185	266	257	47	84	110	0.5
8	135	237	283	34	75	120	0.6
8.5	114	204	285	29	64	121	0.7
9	72	164	251	18	52	107	0.8
9.5	37	101	221	9	32	94	0.9
10	43	30	91	3	10	38	1.0
Total	3978	3172	2346	4000	4000	4000	

this may be done by simply assuming the denotation as given in the last column of Table II.

In the second place the frequencies corresponding to the extreme limits must be excluded from the calculation because they must be considered as representing peculiar meteorological conditions and also because they cannot be taken as representing average values between ∓ 1.05 and ∓ 0.95 in the same sense as any other group.

Therefore, in calculating the constants of frequency-formulae, these extreme values are omitted and the remaining frequencies again reduced to a total of 1000.

2. In the first place the frequency-formula known as Type I of Prof. PEARSON'S formulae finds an application :

$$u = \mathfrak{A} \left(1 + \frac{x}{p} \right)^a \left(1 - \frac{x}{q} \right)^b$$

which, for the assumed conditions and choice of origin, takes the simple form :

$$u = \mathfrak{A} (1 + x)^a (1 - x)^b \dots \dots \dots (1)$$

and can be regarded as a generalization of the condition that the function vanishes for $x = \pm 1$.

Its constants may be calculated from the following relations :

$$\mathfrak{A} = \frac{1}{2^{a+b+1}} \frac{\Gamma(a+b+2)}{\Gamma(a+1)\Gamma(b+1)} \dots \dots \dots (2)$$

$$\frac{(\mu + 1)^{(n)}}{(\mu + 1)^{(n-1)}} = \frac{2(a+n)}{a+b+n+1} \dots \dots \dots (3)$$

where

$$(\mu + 1)^{(n)} \mu_n + n \mu_{n-1} + \frac{n(n-1)}{2!} \mu_{n-2} + \text{etc.}$$

and μ_n represents the mean of the n^{th} order.

As, besides \mathfrak{A} , by which the area of the curve is defined as equal to unity, only two constants appear in formula (1) as characteristics of the curve, it is sufficient to calculate the means of the first and second order μ_1 and μ_2 .

Putting

$$p = 1 - \mu_1, \quad q = \frac{1 - \mu_2}{1 + \mu_1},$$

we find :

$$a + 1 = \frac{(2 - p)q}{2(p - q)}, \quad b + 1 = \frac{pq}{2(p - q)} \dots \dots \dots (4)$$

This formula offers the advantage that, the constants a and b being known, a simple expression can be given for the situation of the maximum-value :

$$x_m = \frac{a - b}{a + b}.$$

In the second place we have to consider the expression in series-form proposed by the author in an earlier publication¹⁾, which may be regarded as a generalized zonal function, modified according to the condition :

¹⁾ These Proceedings Vol. X. (799—817).

$$u = 0 \text{ for } x = \pm 1.$$

$$u = \sum A'_n R_{n+2} \dots \dots \dots (5)$$

$$R_{n+2} = (x^2-1) R'_n = (x^2-1) \left[x^n - \frac{n(n-1)}{2 \cdot (2n+1)} x^{n-2} + \right. \\ \left. + \frac{n(n-1)(n-2)(n-3)}{2 \cdot 4 \cdot (2n+1)(2n-1)} x^{n-4} - \text{etc.} \right]$$

$$A'_n = \beta \left[\mu_n - \frac{n(n-1)}{2 \cdot (2n+1)} \mu_{n-2} + \frac{n(n-1)(n-2)(n-3)}{2 \cdot 4 \cdot (2n+1)(2n-1)} \mu_{n-4} - \text{etc.} \right] \cdot (6)$$

$$\beta = - \frac{(2n+3)(2n+1)!(2n+1)!}{2^{2n+1}(n+2)!n!n!} \dots \dots (7)$$

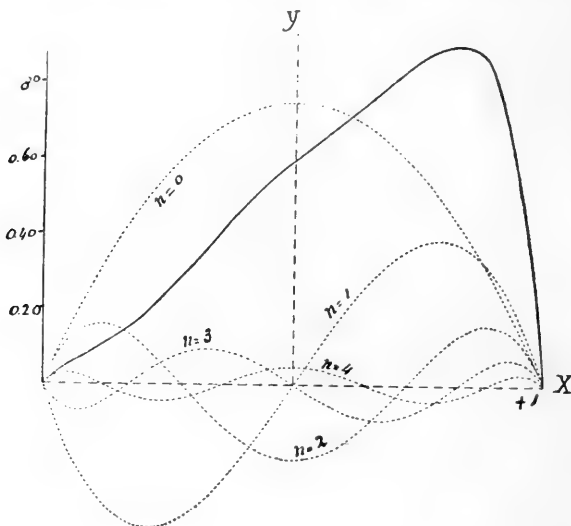
$$\mu_n = \int_{-1}^{+1} u x^n dx.$$

The use of the proposed series enables us to introduce more constants than two, which, in this case, is a decided advantage as the means of higher order necessarily decrease and, therefore, the convergency is assured.

For the position of the maximum-value however no definite expression can be derived from these formulæ, and it has to be determined by approximative methods.

Values of the function R_{n+2} for $n=0$ to $n=4$ have been calculated and are given in Table X; for the first term, which remains the same for all curves, $A_0 R_2$ has been given instead of R_2 .

The figure represents the way in which a frequency-curve (full



line) according to this formula is constructed out of its constituents (broken line) for the case:

$$A_1 = A_2 = A_3 = A_4 = 1,$$

so that the ordinates of the curve are found simply by taking together the 5 columns of Table X.

3. The following constants of formulae (1) and (5) are deduced from the data given in Table II (2nd part), the frequencies for a cloudiness 0 and 10 being omitted and the total reduced to 1000. For reasons to be given furtheron, the values of the A_n constants are not quite in conformity with the expression (6), the sign being inverted and the values divided by $n + 3$, so that;

$$(n + 3) A_n = - A'_n$$

I. East-Monsoon.

$\mu_1 = -0.0554$	$A_1 = -0.0519$	$\mathfrak{A} = 0.8416$
$\mu_2 = +0.1690$	$A_2 = -0.1017$	$a = 1.3654$
$\mu_3 = -0.0095$	$A_3 = +0.1631$	$b = 1.6428$
$\mu_4 = +0.0631$	$A_4 = -0.0650$	

II. Months of Transition.

$\mu_1 = 0.2136$	$A_1 = +0.2003$	$\mathfrak{A} = 0.7486$
$\mu_2 = 0.1999$	$A_2 = -0.0003$	$a = 2.1470$
$\mu_3 = 0.0921$	$A_3 = +0.0069$	$b = 1.0393$
$\mu_4 = 0.0859$	$A_4 = +0.0081$	

III. West-Monsoon.

$\mu_1 = 0.4545$	$A_1 = +0.4261$	$\mathfrak{A} = 0.4326$
$\mu_2 = 0.3191$	$A_2 = +0.3901$	$a = 3.4001$
$\mu_3 = 0.2173$	$A_3 = +0.2584$	$b = 0.6502$
$\mu_4 = 0.1683$	$A_4 = +0.1299$	

In the constants of either formula the differences characteristic for the different seasons are well marked.

4. In order to examine in how far the results of the computation by means of the frequency-formulae agree with the data, we have to integrate the expressions between the limits x and -1 .

For the formula (5) in seriesform this offers no difficulty; from the differential equation:

$$(x^2 - 1) \frac{d^2 R_{n+2}}{dx^2} = (n + 2)(n + 1) R_{n+2}$$

we readily find:

$$I'_n = \int_{-1}^x R_{n+2} dv = \frac{(x^2-1)^2}{n+3} \cdot \frac{1}{n} \frac{dR'_u}{dx} \dots \dots (8)$$

from which, the R'_n function being known, we easily derive the expressions (10). Formula (8) holds good for all values of n except $n = 0$, in which case:

$$I'_0 = \frac{x^3 - 3x - 2}{3} \dots \dots \dots (9)$$

The A_n coefficients, calculated by formula (6) being comparatively large and the values computed by (8) small, it is desirable to omit the factor $(n + 3)$ in (8) and (9) and to divide the expression for A_n by the same quantity; at the same time the sign of β , and therefore also the signs of (8) and (9), can be changed.

With these premises the integrals assume the form:

$$\left. \begin{aligned} I_0 &= x(1-x^2) + 2(1+x) \\ I_1 &= -(1-x)^2 \\ I_2 &= I_1 x \\ I_3 &= I_1 \left(x^2 - \frac{1}{7} \right) \\ I_4 &= I_1 x \left(x^2 - \frac{1}{3} \right) = I_2 \left(x^2 - \frac{1}{3} \right) \end{aligned} \right\} \dots \dots (10)$$

Numerical values of these integrals calculated for values of x increasing by 0.05 are given in Table IX; in the first column, which remains the same for curves of different description, instead of I_0 , the product $A_0 I_0$ has been given.

Integrating formula (1) between the limits x and -1 , we encounter the difficulty that, putting:

$$x = 2z - 1$$

and developing, we obtain the form:

$$\int_{-1}^x u dx = \frac{a+b+1}{2} \mathfrak{A} \left[\frac{z^{a+1}}{a+1} - b \frac{z^{a+2}}{a+2} + \frac{b(b-1)}{2!} \frac{z^{a+3}}{a+3} - \text{etc.} \right]$$

which, evidently, for large values of z slowly converges, so that a considerable number of terms have to be taken into account if, as is necessary in our case, we desire to determine the values with an accuracy up to the third decimal.

Other forms of development are of course possible, but I have not succeeded in finding less laborious expressions.

5. As, owing to this difficulty, the computations necessary for the testing of the formulae had to be restricted, the frequencies of Table II have been aggregated between wider limits: Table III exhibits these frequencies reduced to a total of 1000; in the first part for all data, in the second part with the omission of frequencies for a cloudiness 0 and 10. It is this series which has to be compared with the results of the calculation.

TABLE III.

	I	II	III	I	II	III
-1.00 tot -0.75	23	5	0	23	5	0
-0.75 „ -0.55	90	23	8	90	23	8
-0.55 „ -0.35	148	63	14	149	64	15
-0.35 „ -0.15	187	104	30	188	105	31
-0.15 „ 0.05	174	137	73	175	138	76
0.05 „ 0.25	131	170	118	131	172	123
0.25 „ 0.45	107	181	167	107	183	174
0.45 „ 0.65	81	159	230	81	161	239
0.65 „ 0.85	47	116	228	47	117	237
0.85 „ 1.00	12	42	132	9	32	97

The results of the computation according to formula (5) are given in Table IV.

TABLE IV. I. East-Monsoon.

	A_1I_1	A_2I_2	A_3I_3	A_4I_4	A_0I_0 + total
-1 00 tot -0.75	0.0099	-0.0146	-0.0131	-0.0021	0.0231
-0.75 „ -0.55	0.0153	-0.0126	0.0004	0.0026	0.0917
-0.55 „ -0.35	0.0147	-0.0002	0.0151	0.0032	0.1520
-0.35 „ -0.15	0.0096	0.0128	0.0164	-0.0008	0.1781
-0.15 „ +0.05	0.0021	0.0196	0.0040	-0.0040	0.1708
+0 05 „ +0.25	-0.0060	0.0173	-0.0113	-0.0028	0.1433
+0.25 „ +0.45	-0.0126	0.0068	-0.0177	0.0015	0.1091
+0.45 „ +0.65	-0.0157	-0.0071	-0.0090	0.0037	0.0760
+0.65 „ +0 85	-0.0133	-0.0154	0.0079	0.0004	0.0447
+0.85 „ +1.00	-0.0040	-0.0067	0.0073	-0.0017	0.0109

TABLE IV. II. Transition.

	A_1I_1	A_2I_2	A_3I_3	A_4I_4	A_5I_5 + total
-1.00 tot -0.75	-0.0383	0.0000	-0.0006	0.0003	0.0044
-0.75 " -0.55	-0.0591	0.0000	0.0000	-0.0003	0.0267
-0.55 " -0.35	-0.0568	0.0000	0.0006	-0.0004	0.0625
-0.35 " -0.15	-0.0372	0.0000	0.0007	0.0001	0.1037
-0.15 " +0.05	-0.0079	0.0001	0.0002	0.0005	0.1420
+0.05 " +0.25	0.0233	0.0001	-0.0005	0.0003	0.1693
+0.25 " +0.45	0.0487	0.0000	-0.0007	-0.0002	0.1789
+0.45 " +0.65	0.0606	0.0000	-0.0004	-0.0005	0.1638
+0.65 " +0.85	0.0514	0.0000	0.0003	0.0000	0.1168
+0.85 " +1.00	0.0154	0.0000	0.0003	0.0002	0.0319

TABLE IV. III. West-Monsoon.

	A_1I_1	A_2I_2	A_3I_3	A_4I_4	A_5I_5 + total
-1.00 tot -0.75	-0.0816	0.0561	-0.0208	0.0043	0.0010
-0.75 " -0.55	-0.1257	0.0484	0.0007	-0.0053	0.0042
-0.55 " -0.35	-0.1208	0.0007	0.0241	-0.0063	0.0168
-0.35 " -0.15	-0.0790	-0.0493	0.0257	0.0016	0.0391
-0.15 " +0.05	-0.0168	-0.0754	0.0064	0.0079	0.0712
+0.05 " +0.25	0.0495	-0.0664	-0.0179	0.0056	0.1169
+0.25 " +0.45	0.1035	-0.0260	-0.0281	-0.0029	0.1776
+0.45 " +0.65	0.1289	0.0271	-0.0143	-0.0074	0.2384
+0.65 " +0.85	0.1093	0.0591	0.0126	-0.0008	0.2453
+0.85 " +1.00	0.0328	0.0256	0.0115	0.0033	0.0892

Table V shows the differences between the results of the observation O (Table III 2nd part) and of the computation C (Table IV last column).

TABLE V. $\Delta = O - C$, formula in seriesform.

	I. East-Monsoon	II. Transition	III. West-Monsoon.
-1.00 tot -0.75	0	1	-1
-0.75 „ -0.55	-2	-4	4
-0.55 „ -0.35	-3	1	-2
-0.35 „ -0.15	10	1	-8
-0.15 „ 0.05	4	-4	5
0.05 „ 0.25	-12	3	6
0.25 „ 0.45	-2	4	-4
0.45 „ 0.65	5	-3	1
0.65 „ 0.85	2	0	-8
0.85 „ 1.00	-2	0	8
$\sqrt{\frac{\Delta^2}{n}}$	5.57	2.63	5.39

The question whether or not PEARSON'S formula (1) leads to an equally satisfactory result can be readily answered by supposing formula (1) to be expanded according to formula (5). Then, of course, the coefficients A_1 and A_2 will be the same whether calculated directly or with the help of a and b and, as the fourth term plays an unimportant part, all depends upon the third term which is determined by the mean of the third order μ_3 .

If by means of (3) we calculate μ_3 from a and b , we find:

	observed	calculated by (3)	observed	calculated by (3)
East-Monsoon $\mu_3 =$	-0.0095	-0.0225	$\mu_4 =$ 0.0631	0.0641
Transition „ =	0.0921	0.0902	„ = 0.0859	0.0856
West-Monsoon „ =	0.2173	0.3219	„ = 0.1683	0.1917

From this we may conclude that, for the months of transition formula (1) will lead to excellent results; for the West-Monsoon the agreement will be satisfactory; but for the East-Monsoon rather large discrepancies are to be expected.

TABLE VI. $\Delta = O - C$, formula Pearson.

	I East-Monsoon	II Transition	III West-Monsoon
-1.00 tot -0.75	-13	- 1	0
- 0.75 " -0.55	- 1	- 4	4
-0.55 " -0.35	12	3	0
-0.35 " -0.15	25	3	7
-0.15 " 0.05	6	- 2	0
0.05 " 0.25	-25	2	- 2
0.25 " 0.45	-18	2	- 7
0.45 " 0.65	- 1	- 5	12
0.65 " 0.85	10	1	4
0.85 " 1.00	5	1	- 4
$\sqrt{\frac{\Delta^2}{n}}$	14.32	2.72	5.42

The differences given in Table VI confirm this expectation as well as the computation of the position of the maximum-value.

Position of maximum-values.

	Observed Table II.	Calculated form. PEARSON	Calculated form. series
East-Monsoon	-0.25	-0.09	-0.20
Transition	0.30	0.35	0.35
West-Monsoon	0.65	0.90	0.65

The use of frequency-formulae with two constants will, therefore, give satisfactory results only in those cases where the curve is of a comparatively simple construction or if, by chance, μ_3 (or A_3) as calculated by means of a and b , are approximately equal to the observed values.

Moreover, as the constants appear in exponential form, it will be difficult to calculate Tables for the function and its integrals as p and q may assume all possible values and occur in an infinite number of combinations.

Constants for every month computed according to both formulae from the data of Table I with the omission of the extreme values are given in Tables VII and VIII.

TABLE VII.
 Constants of formula (5).

	A_1	A_2	A_3
January	0.4293	0.4118	0.3514
February	0.4247	0.3957	0.2653
March	0.2962	0.0847	-0.0207
April	0.1481	-0.01385	-0.0792
May	0.0114	-0.1572	0.0609
June	-0.0003	-0.1939	0.0988
July	-0.0672	-0.0758	0.1769
August	-0.1330	-0.1093	0.2607
September	-0.0548	-0.1509	0.2963
October	0.0724	-0.0735	0.0885
November	0.2747	0.0961	0.0425
December	0.3795	0.2530	0.1355

TABLE VIII.
 Constants of formula Pearson, Type I.

	η	a	b
January	0.420	3.242	0.577
February	0.436	3.278	0.611
March	0.656	3.041	1.101
April	0.880	2.671	1.670
May	0.922	1.824	1.756
June	0.924	2.049	2.050
July	0.798	1.225	1.568
August	0.831	1.439	2.246
September	0.894	1.645	1.974
October	0.813	1.573	1.204
November	0.664	2.475	0.900
December	0.534	3.484	0.900

TABLE IX. Values of I_n .

x	$A_0 I_0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$
-1.00	0.0000	0.0090	0.0000	0.0000	0.0000
-0.95	0.0018	-0.0095	0.0090	-0.0072	0.0051
-0.90	0.0073	-0.0361	0.0325	-0.0241	0.0155
-0.85	0.0160	-0.0770	0.0655	-0.0446	0.0255
-0.80	0.0280	-0.1396	0.1037	-0.0644	0.0318
-0.75	0.0430	-0.1914	0.1436	-0.0803	0.0329
-0.70	0.0608	-0.2601	0.1821	-0.0903	0.0285
-0.65	0.0812	-0.3335	0.2168	-0.0933	0.0193
-0.60	0.1040	-0.4096	0.2458	-0.0889	0.0066
-0.55	0.1291	-0.4865	0.2676	-0.0777	-0.0082
-0.50	0.1563	-0.5625	0.2813	-0.0602	-0.0234
-0.45	0.1853	-0.6360	0.2862	-0.0379	-0.0374
-0.40	0.2160	-0.7056	0.2822	-0.0121	-0.0489
-0.35	0.2482	-0.7700	0.2695	0.0147	-0.0568
-0.30	0.2818	-0.8281	0.2484	0.0438	-0.0604
-0.25	0.3164	-0.8789	0.2197	0.0707	-0.0595
-0.20	0.3520	-0.9216	0.1843	0.0948	-0.0541
-0.15	0.3884	-0.9555	0.1433	0.1150	-0.0445
-0.10	0.4253	-0.9801	0.0980	0.1303	-0.0317
-0.05	0.4625	-0.9950	0.0498	0.1397	-0.0165
0.00	0.5000	-1.0000	0.0000	0.1429	0.0000
0.05	0.5375	-0.9950	-0.0498	0.1397	0.0165
0.10	0.5748	-0.9801	-0.0980	0.1303	0.0317
0.15	0.6117	-0.9555	-0.1433	0.1150	0.0445
0.20	0.6480	-0.9216	-0.1843	0.0948	0.0541
0.25	0.6836	-0.8789	-0.2197	0.0707	0.0595
0.30	0.7183	-0.8281	-0.2485	0.0438	0.0604
0.35	0.7518	-0.7700	-0.2695	0.0147	0.0568
0.40	0.7840	-0.7056	-0.2832	-0.0121	0.0489
0.45	0.8147	-0.6360	-0.2862	-0.0379	0.0374
0.50	0.8438	-0.5625	-0.2813	-0.0602	0.0234
0.55	0.8709	-0.4865	-0.2676	-0.0777	0.0082
0.60	0.8960	-0.4096	-0.2458	-0.0889	-0.0066
0.65	0.9189	-0.3335	-0.2168	-0.0933	-0.0193
0.70	0.9393	-0.2601	-0.1821	-0.0903	-0.0285
0.75	0.9570	-0.1914	-0.1436	-0.0803	-0.0329
0.80	0.9720	-0.1296	-0.1037	-0.0644	-0.0318
0.85	0.9840	-0.0770	-0.0655	-0.0446	-0.0255
0.90	0.9928	-0.0361	-0.0325	-0.0241	-0.0155
0.95	0.9982	-0.0095	-0.0090	-0.0072	-0.0051
1.00	1.0000	0.0000	0.0000	0.0000	0.0000

TABLE X. Values of the function R_{n+2} .

x	$A_1 R_2$	$n=1$	$n=2$	$n=3$	$n=4$
1.00	0.0000	0.0000	0.0000	0.0000	0.0000
-0.95	0.0731	-0.0926	0.0685	-0.0439	0.0254
-0.90	0.1425	-0.1710	0.1159	-0.0652	0.0314
-0.85	0.2081	-0.2359	0.1450	-0.0693	0.0244
-0.80	0.2700	-0.2880	0.1584	-0.0609	0.0110
-0.75	0.3281	-0.3281	0.1586	-0.0439	-0.0048
-0.70	0.3825	-0.3570	0.1479	-0.0219	-0.0199
-0.65	0.4331	-0.3754	0.1285	0.0023	-0.0321
-0.60	0.4800	-0.3840	0.1024	0.0263	-0.0402
-0.55	0.5231	-0.3836	0.0715	0.0484	-0.0436
-0.50	0.5625	-0.3750	0.0375	0.0670	-0.0424
-0.45	0.5981	-0.3589	0.0020	0.0811	-0.0370
-0.40	0.6300	-0.3360	-0.036	0.0902	-0.0281
-0.35	0.6581	-0.3071	-0.0680	0.0940	-0.0167
-0.30	0.6825	-0.2730	-0.1001	0.0924	-0.0039
-0.25	0.7031	-0.2344	-0.1289	0.0858	0.0092
-0.20	0.7200	-0.1920	-0.1536	0.0746	0.0217
-0.15	0.7331	-0.1466	-0.1735	0.0595	0.0324
-0.10	0.7425	-0.0990	-0.1881	0.0414	0.0406
-0.05	0.7481	-0.0499	-0.1970	0.0213	0.0458
0.00	0.7500	0.0000	-0.2000	0.0000	0.0476
0.05	0.7481	0.0499	-0.1970	-0.0213	0.0458
0.10	0.7425	0.0990	-0.1881	-0.0414	0.0406
0.15	0.7331	0.1467	-0.1735	-0.0595	0.0324
0.20	0.7200	0.1920	-0.1536	-0.0746	0.0217
0.25	0.7031	0.2344	-0.1289	-0.0858	0.0092
0.30	0.6825	0.2730	-0.1001	-0.0924	-0.0039
0.35	0.6581	0.3071	-0.0680	-0.0940	-0.0167
0.40	0.6300	0.3360	-0.0336	-0.0902	-0.0281
0.45	0.5981	0.3589	0.0020	-0.0811	-0.0370
0.50	0.5625	0.3750	0.0375	-0.0670	-0.0424
0.55	0.5231	0.3836	0.0715	-0.0484	-0.0436
0.60	0.4800	0.3840	0.1024	-0.0263	-0.0402
0.65	0.4331	0.3754	0.1285	-0.0023	-0.0321
0.70	0.3825	0.3570	0.1479	0.0219	-0.0199
0.75	0.3281	0.3281	0.1586	0.0439	-0.0048
0.80	0.2700	0.2880	0.1584	0.0609	0.0110
0.85	0.2081	0.2359	0.1450	0.0693	0.0244
0.90	0.1425	0.1710	0.1159	0.0652	0.0314
0.95	0.0731	0.0926	0.0685	0.0439	0.0254
1.00	0.0000	0.0000	0.0000	0.0000	0.0000

Mathematics. — “On fourdimensional nets and their sections by spaces.” (Third part.) By Prof. P. H. SCHOOTE.

The net (C_{16}).

1. In the first part of this investigation we have found that the net (C_{16}) of cells $C_{16}^{(2V^2)}$ is formed out of three equally strongly developed groups of homothetic cells $C_{16}^{(2V^2)}$, one group of erect cells $C_{16}^{(2V^2)}$ polarly inscribed in eightcells $C_8^{(4)}$ and two groups of inclined cells $C_{16}^{(2V^2)}$ and $C_{16}^{(2V^2)}$ bodily inscribed in eightcells $C_8^{(2)}$, namely the *positive* group and the *negative* one. If we restrict ourselves once more, with respect to this net, to the sections by spaces normal to one of the four different axes of one of the sixteencells, it is evident from the table of connections between these different axes given in the first part (p. 544) — if we bear in mind that the three groups of cells of the net are equivalent — that we have only to consider three series of parallel intersecting spaces, viz. those normal to one of the axes OR_8, OF_8, OK_8 of the circumscribed eightcells. In these three cases, corresponding successively to the fifth, the fourth, and the third line of the quoted table, we find indeed for the erect sixteencells series of spaces normal to OE_{16}, OK_{16} and OF_{16} , whilst the first of the three cases provides us, for the inclined sixteencells, with a series of spaces normal to OR_{16} . So all in all we have to bring to light three different threedimensional space-fillings and their transformation connected with a parallel motion of the intersecting space. But in order to do this we have to consider more than the four usual series of intersecting spaces respectively normal to an axis $OE_{16}, OK_{16}, OF_{16}, OR_{16}$; for the spaces normal to OK_8 presenting themselves in the last of the three cases are not normal to any one of the four axes of the *inclined* sixteencells but to the line connecting the centre of one of these cells with the point characterized by the coordinates (3, 1, 1, 1) with respect to the system of coordinates with the four axes OE_{16} of that cell as axes. So all in all we have to deal with five series of parallel intersecting spaces which may be characterized by the symbols (1,0,0,0), (1,1,0,0), (1,1,1,0), (1,1,1,1), (3,1,1,1), as they are always normal to the diameter of the cell passing through the point the coordinates of which with respect to the axes OE_{16} of the cell are given by the corresponding symbol.

2. In the same way as we have done this in our second com-

inunication for the six series of parallel sections of the eightcell we indicate the results of the intersection of a single sixteencell $C_{16}^{(2\sqrt{2})}$ in two different manners. A first plate will give the projections of the limiting elements of the sixteencell on the diameter normal to the intersecting spaces, which will enable us to deduce the sections from it tabularly; a second plate will give the sections themselves in parallel perspective, included in the sections with the polarly circumscribed $C_8^{(4)}$ or the bodily circumscribed $C_8^{(2)}$. Moreover a third plate will contain two groups of diagrams, the first of which will elucidate the manner of deduction of the projections given on plate I, whilst the second is concerned with the space-fillings obtained by the intersection of the net (C_{16}). In order to facilitate the survey of these space-fillings we deviate from the way followed in the second communication and treat together the more or less regular space-fillings presenting themselves here, instead of joining each of them separately to the corresponding generating three series of intersecting spaces.

We now first consider the four diagrams of the first group of plate III dominating the deduction of the projections of plate I. In fig. 1 we once more show how the inclined cell $C_{16}^{(2\sqrt{2})}$, indicated by its vertices only, is inscribed in the cell $C_8^{(2)}$. If we indicate by A, B, C, D the vertices of one of the sixteen limiting bodies, by A', B', C', D' the opposite ones, the sixteen limiting tetrahedra are

		$A'B'CD$		
$ABCD$	$A'BCD$	$A'BC'D$	$AB'C'D'$	
	$AB'CD$	$A'BCD'$	$A'BC'D'$	
	$ABC'D$	$AB'C'D$	$A'B'C'D'$	
	$ABCD'$	$A'BCD'$	$A'B'C'D'$	
		$ABC'D'$		$A'B'C'D'$

Of these five groups of 1, 4, 6, 4, 1 tetrahedra those of the first, the third, and the fifth groups are inscribed in the eight limiting cubes of the eightcell, whilst the four vertices of each of the tetrahedra of the second and the fourth group always split up with reference to two opposite limiting cubes of the eightcell into one vertex and three vertices.

With reference to the system of coordinates $O(Y_1, Y_2, Y_3, Y_4)$ of the four diagonals AA', BB', CC', DD' already used in the first communication the five series of parallel sections are characterized by the symbols $(1, 0, 0, 0)$, $(1, 1, 0, 0)$, $(1, 1, 1, 0)$, $(1, 1, 1, 1)$, $(3, 1, 1, 1)$ mentioned above, from which can be deduced that the octuple of vertices of the sixteencell projects itself on the chosen axis of projection in these five cases in arrangements indicated by $(1, 6, 1)$, $(2, 4, 2)$, $(3, 2, 3)$, $(4, 4)$, $(1, 3, 3, 1)$. Of these five cases the first and the fourth are evident by themselves; so the parts of plate I bearing the headings $(1, 0, 0, 0) OE_{16}$ and $(1, 1, 1, 1) OR_{16}$ can be understood immediately. The three other cases can be explained by the three following diagrams, a common characteristic of which is that the eight vertices of the sixteencell have been obtained by starting from the cube that is found by intersecting the eightcell of fig. 1 by the central space normal to AA' , by splitting up the eight vertices of that cube into the two sets of vertices of bodily inscribed tetrahedra and by erecting normals on the space bearing that cube — i. e. by drawing in the diagram in parallel perspective lines parallel to AA'' — the length of which is equal to $\frac{1}{2} AA''$, in the vertices of one of the tetrahedra to one side and in the vertices of the other tetrahedron to the opposite side. This representation of the cube with the two quadruples of points $ABCD, A'B'C'D'$ has been repeated in three different positions by a motion parallel to itself from left to right and from above to below over the same distance, which gives rise to the three diagrams 2, 3, 4 which we will now examine one after another.

In fig. 2 the eight vertices of the sixteencell have been projected on to the line $F_s F'_s$, joining the midpoints of two opposite edges of the cube and forming therefore an axis OF_s of the eightcell; on this axis the vertices A, B project themselves in F_s , the vertices C, D, C', D' in O and the vertices A', B' in F'_s . We find again here that the axis OF_s of the eightcell is at the same time an axis OK_{16} of the bodily inscribed sixteencell, as F_s is the midpoint of AB , and deduce now from the arrangement $(2, 4, 2)$ of the projections of the vertices all that is indicated on plate I under the heading $(1, 1, 0, 0) OK_{16}$.

In fig. 3 the centres of gravity F_{16}, F'_{16} of the opposite faces $ABC, A'B'C'$ have been determined, and the axis OF_{16} joining these points forms the axis of projection. Then the three vertices A, B, C project themselves in F_{16} , the two vertices D, D' in O , the three vertices A', B', C' in F'_{16} . From the arrangement $(3, 2, 3)$ can then be deduced what appears in plate I under the heading $(1, 1, 1, 0) OF_{16}$.

In fig. 4 the diagonal $D''D'''$ of the cube, forming an axis OK_8 of the eightcell, appears as axis of projection. Here the projection of the eight vertices of the sixteencell on that line $D''D'''$ is found in the easiest way by projecting these points first on to the space of the cube with the diagonal $D''D'''$ and by repeating this for the eight projections obtained with respect to the line $D''D'''$. For, the projections of the eight vertices of the sixteencell on to the space of the cube are the vertices of that cube, and these project themselves on $D''D'''$, if this line is divided by P and P' into three equal parts, according to the arrangement (1, 3, 3, 1) in the points D'', P, P', D''' . From this arrangement (1, 3, 3, 1) of the vertices can be deduced immediately what appears on plate I under the heading (3, 1, 1, 1) OK_8 .

For each of the five cases considered we repeat under the heading "type" the manner in which the four couples of opposite vertices of the eightcell project themselves on the different axes.

3. We now proceed to the description of the sections, represented in parallel perspective on plate II, of the erect $C_{16}^{(2V^2)}$ and its envelope $C_3^{(4)}$ on one side, and the inclined $C_{16}^{(2V^2)}$ and $C_{16}^{(2V^2)}$ and their envelopes $C_8^{(2)}$ on the other. The sections of the C_{16} can be deduced from the tables of projection of plate I, those of the circumscribed $C_8^{(4)}$ and $C_8^{(2)}$ have already been given on plate II of the second communication.

By two thick vertical lines *this* plate II is divided into three parts, respectively related to sections normal to OR_8 , normal to OF_8 , normal to OK_8 . Each of these three parts is divided by a thin vertical line into two columns; of these two columns the lefthand one always contains three sections of erect sixteencells, the righthand one five or more sections of inclined sixteencells. We now consider separately each of the six columns so formed.

Sections normal to OR_8 .

a. *Erect cells.* This case is the simplest of all. If by a motion parallel to itself of the intersecting space normal to the axis OE_{16} of $C_{16}^{(2V^2)}$ the point of intersection of that space with that axis moves from one of the two vertices situated on that axis to the other, the section with the circumscribed $C_8^{(4)}$ remains a cube with edge four and the section with the inscribed $C_{16}^{(2V^2)}$ itself, which is always

a regular octahedron, increases in size from a point, the centre of the cube, to the inscribed octahedron with edge $2\sqrt{2}$ and then it passes through the same stadia in inverse order. Of the three diagrams the second represents an intermediate stadium, in which the edge of the octahedron is $\sqrt{2}$.

b. *Inclined cells.* If the point of intersection of the intersecting space normal to the axis OR_{16} of $C_{16}^{(2\sqrt{2})}$ with this axis describes this axis completely, the section with the bodily circumscribed $C_8^{(2)}$ remains a cube with edge two, whilst the section with the inscribed $C_{16}^{(2\sqrt{2})}$, always a tetrahedron truncated at the vertices and at the edges, transforms itself from a right tetrahedron to a left one in the manner shown by the five diagrams. In the third of the five we recognize the semiregular body (with regular faces) forming the combination of cube and octahedron in equilibrium, whilst the form represented by the second and the fourth show how this combination is formed out of the right tetrahedron and passes into the left one¹⁾.

Sections normal to OF_8 .

a. *Erect cells.* Here a difference arises with respect to the fraction indicating the position of the intersecting space, according as the line through O normal to the intersecting space is considered either as an axis OK_{16} of the inscribed $C_{16}^{(2\sqrt{2})}$ or as an axis OF_8 of the circumscribed $C_8^{(4)}$. Therefore to each of the three diagrams presenting themselves here correspond two fractions, one below at the righthand side referring to the axis OK_{16} , another above at the lefthand side referring to the axis OF_8 . If the point of intersection of the intersecting space with the axis OF_8 of $C_8^{(4)}$ describes this axis completely, the height of the rectangular parallelepipedon forming the section with $C_8^{(4)}$, the base of which is a square with side four, increases from nought to $4\sqrt{2}$ and then again decreases to nought. But only at the moment that this height is increased to $2\sqrt{2}$ does the polarly inscribed $C_{16}^{(2\sqrt{2})}$ begin to be cut. So we find in the three cases, where

1) For the sake of clearness the limiting elements of the section of the cell C_{16} situated in the faces of the section of the enveloping box C_8 have been brought to the fore by indicating the vertices situated in *all* the faces of that envelope as black points, and by shading the faces of the section of the cell C_{16} situated in *visible* faces of that envelope.

the height is respectively $2\sqrt{2}$, $3\sqrt{2}$, $4\sqrt{2}$ and the fractions above to the left are $\frac{2}{8}, \frac{3}{8}, \frac{4}{8}$, for the fractions below to the right $0, \frac{1}{4}, \frac{2}{4}$ and for the sections of $C_{16}^{(2\sqrt{2})}$ an edge, a cube covered at two opposite faces by square pyramids, a square double-pyramid.

b. *Inclined cells.* In the five cases corresponding to the fractions $0, \frac{1}{8}, \frac{2}{8}, \frac{3}{8}, \frac{4}{8}$ the section of the circumscribed $C_8^{(2)}$ is a rectangular parallelepipedon, the base of which is a square with side two, with a height $0, \frac{1}{2}\sqrt{2}, \sqrt{2}, \frac{3}{2}\sqrt{2}, 2\sqrt{2}$ successively. The sections

of the inscribed $C_{16}^{(2\sqrt{2})}$ represented in the first, the third and the fifth of the five figures are equal to those of the preceding column and in the second and the fourth intermediate forms between these; in general the section can be characterized as a rectangular parallelepipedon with a square as base and upperplane, covered at these two faces by square pyramids, the faces of which have a determined inclination.

Sections normal to OK_8 .

a. *Erect cells.* Here too, a difference presents itself as to the fractions, according as the diameter normal to the intersecting space is considered either as an axis OF_{16} or as an axis OK_8 . If the point of intersection of the intersecting space with the axis OK_8 of $C_8^{(4)}$ describes that axis completely, the base of the prismatic section, the height of which remains four, transforms itself in the same manner as the section of a cube with edge four by a plane normal to a diagonal, and now at the moment that this base is increased to a triangle with side $4\sqrt{2}$ a face of the inscribed $C_{16}^{(2\sqrt{2})}$ appears in the intersecting space. So, to the fractions $\frac{4}{12}, \frac{5}{12}, \frac{6}{12}$ above to the left, correspond the fractions $0, \frac{1}{4}, \frac{2}{4}$ below to the right; so we find in the first diagram a triangle in a triangular prism, in the third a regular hexagonal double-pyramid in a regular hexagonal prism, in the second a form (12, 24, 14) bounded by two equilateral triangles, six isosceles triangles, six isosceles trapezia in a semiregular hexagonal prism regular as to the angles.

b. *Inclined cells.* The seven cases corresponding to the fractions $0, \frac{1}{12}, \frac{2}{12}, \dots, \frac{6}{12}$ are all represented here. In the case corresponding to nought the section with $C_8^{(2)}$ is a line, here a vertical one, the section with $C_{16}^{(2\sqrt{2})}$ a point, here the upper extremity of that line. In the cases $\frac{1}{12}, \frac{2}{12}, \frac{3}{12}, \frac{4}{12}$ we find an irregular octahedron, inscribed in a triangular prism, bounded by two equilateral triangles of different size and two sets of three isosceles triangles of different form; the smaller of the two equilateral triangles is always inscribed in the upperplane of the prism, whilst the larger forms a normal section of the prism, successively at the height $\frac{3}{4}, \frac{2}{4}, \frac{1}{4}, 0$. Finally in the cases $\frac{5}{12}, \frac{6}{12}$ we find a semiregular hexagonal prism regular as to the angles and a regular one in which polyhedra (12, 24, 14) are inscribed, once more bounded by two equilateral triangles, six isosceles triangles and six isosceles trapezia. But here, in opposition to the form (12, 24, 14) found above, the two equilateral triangles instead of being homothetic have an opposite orientation. ¹⁾

4. Before we pass to the generation of more or less regular space-fillings by intersecting the net (C_{16}) we wish to say a single word about the diagonal planes appearing in the sections of the cell C_{16} represented on plate II. In my communication "On groups of polyhedra with diagonal planes, derived from polytopes" published in these *Proceedings* of October (p. 277—290) it has been explained that any space intersecting C_{16} and not passing through one of the edges intersects this cell in a polyhedron with the property that through any edge of it passes one and only one diagonal plane, and that we only can obtain sections, through one or more edges of which pass two diagonal planes, if we choose an intersecting space passing through one or more edges of C_{16} . We have especially to show here

¹⁾ In the paper "Regelmässige Schnitte und Projectionen des Achtzelles u.s.w." (Regular sections and projections of the eightcell, the sixteencell, etc.), *Verhandelingen of Amsterdam*, first section, vol. II, N^o. 2, 1894), I restricted myself principally to central sections; I only added incidentally a remark about the sections by spaces not passing through the centre. The figures 11 and 13 of that former paper, being not quite correct, should be replaced by the second figures of the third and fifth columns of plate II of this study.

why this particularity — as was already stated there — does not present itself in any of the sections of the four principal groups.

A mere inspection of plate II is sufficient to show, that *all* the sections of C_{16} represented there — not only those related to the axes OE_{16} , OK_{16} , OF_{16} , OR_{16} but also those of the last column — agree with one another in this, that any edge is situated in one and only one diagonal plane, moving parallel to itself if the intersecting space displaces itself parallelly. As an example we fix our attention on the figures of the fourth column, where a hexagon $MABNCD$ starts on half its journey as a line MN to end it as a lozenge $MANC$.

Now the reason, *why* no edge situated in two diagonal planes occurs here in the cases of sections by spaces containing edges of C_{16} , can be derived from plate I. It comes to this, that spaces through edges of C_{16} , not leaving that cell entirely on one side, do not present themselves for sections normal to OR_{16} or OF_{16} , that they pass through the centre O for sections normal to OE_{16} or OK_{16} and contain a face of C_{16} for sections under the heading $(3, 1, 1, 1)OK_8$. If the intersecting space — see fig. 2 of the communication of October — contains not only the edge AB but also the centre O of the cell, the two points of intersection S_{13}, S_{24} coincide in O , and instead of two diagonal planes ABS_{13}, ABS_{24} we find only one diagonal plane ABO , containing also the edge $A'B'$ opposite to AB and therefore intersecting the section in a square; this happens in the cases of the last figures of the first and the third column of plate II, for the first column with each, for the third column with only one diagonal plane, represented horizontally. In the case of the last column corresponding to the fractional symbol $\frac{4}{12}$ the triangle OPQ forming the base of the section is a face of C_{16} ; so through any side of this triangle passes only one diagonal plane.

5. In order to determine the threedimensional space-fillings generated by intersection of the net (C_{16}) we can follow different ways, some of which are of a more theoretic, others of a more practical character. Those of the first group correspond in this, that we deduce from the section of a determined C_{16} with the intersecting space how this space must affect the other cells of the net (C_{16}). So we can project the axes of all the cells, normal to the intersecting space, on the \bar{x} -axis taken as axis of projection, and deduce from the fraction corresponding to the chosen C_{16} the fraction corresponding to any other cell of the net; this method has been applied to the

net (C_3) in the second communication, and it can be of great service here, as the cells $C_8^{(2)}$ bodily circumscribed to the inclined cells $C_{1,6}$ form a net (C_3) . However, it often proves to be more practical to start from any section presenting itself, to hunt for other sections, possible in the position of the intersecting space under consideration, admitting a face agreeing in shape and in size with one of the faces of the chosen section, and to investigate if it is possible to arrive in this manner at a space-filling either by these two polyhedra only or by means of still more forms equally possible.

Space-fillings normal to OR_8 . Let us imagine in threedimensional space a net of cubes with edge two, built up by cubes alternately white and black so as to form a threedimensional chessboard, with an infinite number of cubes, and let us describe in all white cubes a righthanded, in all black cubes a lefthanded tetrahedron. Then the interstitial spaces between these tetrahedra can be filled up by regular octahedra, forming with the tetrahedra the mixed net of tetrahedra and octahedra with common length of edge $2\sqrt{2}$. If we describe in all white cubes the tetrahedra truncated at vertices and edges of the second, in all black cubes the tetrahedra truncated at vertices and edges of the fourth of the five figures of the second column of plate II, the interstitial spaces can be filled up by regular octahedra of two different sizes, i.e. with edges $\frac{1}{2}\sqrt{2}$ and $\frac{3}{2}\sqrt{2}$. If we describe in *all* cubes the combination of cube and octahedron in equilibrium represented by the third of the five figures, the remaining interstitial spaces can be once more filled by regular octahedra of the same size, this time with the edge $\sqrt{2}$. These generally known results are obtained immediately by means of the method of juxtaposition, if we only bear in mind that two bodily inscribed sixteencells, the boxes $C_8^{(2)}$ of which have a limiting cube in common, are cut by any space normal to the space of that cube in polyhedra being one another's mirror-image with respect to the plane of intersection as mirror, from which it ensues immediately that of the five figures of the second column the first and the fifth correspond to one another, also the second and the fourth, whilst the third stands for itself. By the juxtaposition, which comes here to the filling up of the interstitial spaces, we then find that the two extreme figures of the second column are to be combined with the two extreme figures of the first column, that the middle figure of the second column demands the middle figure of the first column, whilst the two

remaining figures of the second column correspond to two intermediate sections with the fractions $\frac{1}{8}$ and $\frac{3}{8}$ of the first column, not represented here.

If the point O (fig. 5) is the centre and OR an axis OR_s of one of the cells $C_8^{(2)}$ and we assume on the line which is to be considered as axis of projection a scale division with O as origin and half the edge of $C_8^{(2)}$ as unit, the vertices of the cells $C_8^{(2)}$ — and therefore also the centres of $C_8^{(4)}$ — project themselves into the points with a distance from O equal to an odd number of integers. If now the projection P of the intersecting space on to this axis lies between the origin and the point 1, and if $1-2x$ represents the distance OP , the section of all the cells $C_8^{(2)}$ corresponds to the fraction x , whilst both the series of $C_8^{(4)}$, the centres of which project themselves into the points -1 and $+1$, correspond to the fractions $y = \frac{x}{2}$ and $y' = \frac{x+1}{2}$. Now as the fraction x of a positively inscribed C_{16} inverts its sign and passes therefore into $1-x$, if this C_{16} is replaced by a negatively inscribed one, the fractions x and $1-x$ of the five figures of the second column belong together and to them correspond the fractions $\frac{1}{2}x$ and $\frac{1}{2}(x+1)$ of the first column. This result is in accordance with the preceding one; moreover it proves that it is preferable to say that the intermediate sections, not represented in the first column, corresponding to the second and the fourth figures of the second column, bear the fractional symbols $\frac{1}{8}$ and $\frac{5}{8}$.

It goes without saying that by the last method is indicated at the same time what the space-filling corresponding to an arbitrary value of x looks like; as this is immediately clear by itself we do not enter into details.

Space-fillings normal to OF_s . The result found above — that of the five figures of the second column those at the same distance from the middle one belong together — holds for this case too. This is proved easily, in a manner independent of preceding considerations, as follows. If PX_1, PX_2, PX_3, PX_4 (fig. 6) are the

four edges of a $C_8^{(2)}$ meeting in a vertex P , if PQ and PR are the squares described on X_1PX_2 and X_3PX_4 and if F, G, O are the centres of these faces and of the eightcell, $FPGO$ is a square and the net (C_8), to which the cell $C_8^{(2)}$ belongs, projects itself on the plane of the square PR as a plane-filling of squares (fig. 7), whilst the intersecting space normal to the diagonal PR of the square projects itself in a normal to that line. We expressed this in the second communication by saying that the problem of the section of a four-dimensional polytope by a threedimensional space has lost here two of its dimensions. If now amongst the lines normal to the diagonal PR line a passes through R , line b passes through the points S_1, T_1 on the sides RS, RT for which $RS_1 = \frac{1}{4} RS, RT_1 = \frac{1}{4} RT$, and line c passes through the midpoints S_2, T_2 of RS, RT , then the position a of the intersecting space corresponds to the first and the fifth figure of the fourth column of plate II, the position b corresponds to the second and the fourth figure, the position c corresponds to the third one.

A second remark refers to the position of the sections obtained in the third and the fourth column. The first and the third figure of the third column are equal to the first and the fifth figure of the fourth column; also the middle figures of the two columns are equal. But there is a difference in position. In the figures of the third column the axis MN of period four is vertical, in the figures of the fourth column this axis MN is horizontal. This is not accidental. As both columns represent the sections with the polarly circumscribed $C_8^{(4)}$ and the bodily circumscribed $C_2^{(8)}$ in the same orientation, it proves that the axes MN of the sections of the erect sixteencells and those of any of the two groups of the inclined sixteencells are normal to one another, from which may be derived that the three axes MN of the sections of three sixteencells, any two of which belong to different groups, are normal to one another by twos. We verify this by proving that the axes MN of the sections of two inclined sixteencells of different kinds are normal to one another. Therefore we remark that the limiting spaces $P(X_1X_3X_4)$ and $P(X_2X_3X_4)$ of fig. 6 are parallel to OF — as the line GP parallel to OF lies in $P(X_3X_4)$ — and so the intersecting spaces normal to OF are normal to those limiting spaces of $C_2^{(8)}$. As the sixteencells inscribed in $C_8^{(2)}$ and in an adjacent $C_8^{(2)}$ are one another's mirror-

image with respect to the limiting space common to the two eightcells, the sections of both the sixteencells with the intersecting space normal to that limiting space are one another's mirror-image with respect to the plane of intersection of intersecting space and limiting space, i.e. with respect to one of the vertical faces of the rectangular square prism that forms the section of $C_8^{(2)}$. As the axis MN of the figures of column four forms an angle of 45° with each of these four faces, it will be normal to its mirror-image.

In the first of the three cases — that of the first and the third figure of the third column — only one polyhedron appears, the square double-pyramid, the base of which is a square with side $2\sqrt{2}$, the height of which also is $2\sqrt{2}$. In the following way it is easily proved that this not entirely regular octahedron can form a space-filling by itself. Let us consider a net of cubes with edge $2\sqrt{2}$ and divide each of these cubes into six equal square pyramids admitting as base one of the faces of that cube and as common vertex the centre of the cube; then the required net is obtained if we join together to a double-pyramid each pair of pyramids standing on the same base; according to the directions of the axes with period four of these pyramids this net consists of three equally strongly developed groups of polyhedra. We remark that the regular octahedron cannot fill space, but that we obtain a polyhedron that does fill space, as has just been proved, by compressing the regular octahedron in such a manner that the distances of the points of the surface from a plane through four of the six vertices are diminished to $\frac{1}{2}\sqrt{2}$ times the original value.

In the third of the three cases — i.e. in that of the middle figure of the five sections of column four — we have again to deal with only one polyhedron, viz. a cube with edge $\sqrt{2}$ bearing on two opposite faces a square pyramid with height $\frac{1}{2}\sqrt{2}$. We show easily that this body has the space-filling property as follows. Let us start from a net of cubes with edge $\sqrt{2}$ and suppose the centre of one of these cubes to be the origin of a rectangular system of coordinates the axes of which are parallel to the edges of the cube. Then let us divide into six equal square pyramids each cube the centre of which has for coordinates either only even or only odd multiples of $\sqrt{2}$, and join each of these pyramids to the adjacent cube; then the required space-filling is obtained. Of these the two figures 8^a and 8^b show the sections with planes $u=2k\sqrt{2}$ and $u=(2k+1)\sqrt{2}$, where u stands for any of the three coordinates; here have been indicated the fibres of the combination (10, 20, 12) running in the

direction of the axis with period four, whilst sections normal to the axis are characterized by yearnings and medullary rays.

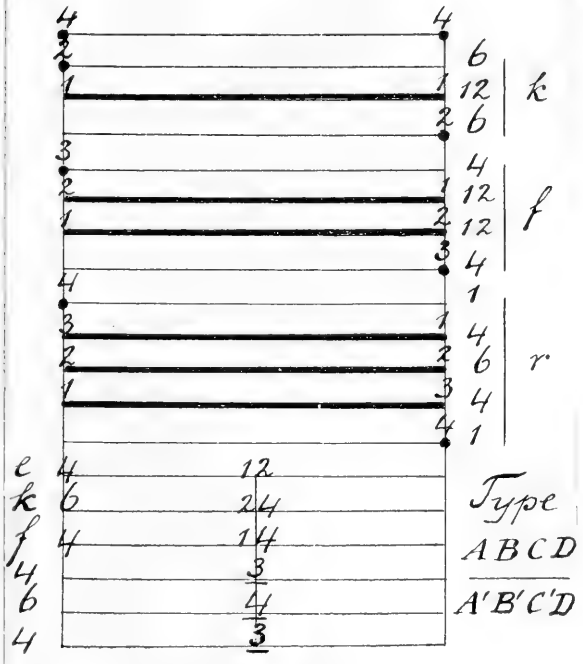
If we wish to treat in an analogous manner the second case — i.e. that of the second and the fourth figure of column four — we can start from a net of cubes with edge $2\sqrt{2}$. If we transform this net by assuming inside these cubes concentric and homothetic cubes with edge $\frac{3}{2}\sqrt{2}$ we find, by omitting the boundaries of the original cubes and producing the boundaries of the new ones, a mixed space-filling by cubes and rectangular parallelepipeda characterized by the triplets of edges $(1, 1, 1)$, $(3, 3, 3)$ and $(1, 1, 3)$, $(1, 3, 3)$ with $\frac{1}{2}\sqrt{2}$ as unit. By splitting up each of the cubes of the two sizes into six equal pyramids and joining these pyramids to the adjacent parallelepipeda we get the required space-filling. Here for clearness' sake the figures 9^a and 9^b show the sections corresponding to those of 8^a and 8^b .

In general the space-filling presenting itself here consists of two different polyhedra occurring in three different orientations; in two particular cases one finds however only one polyhedron occurring in three different positions.

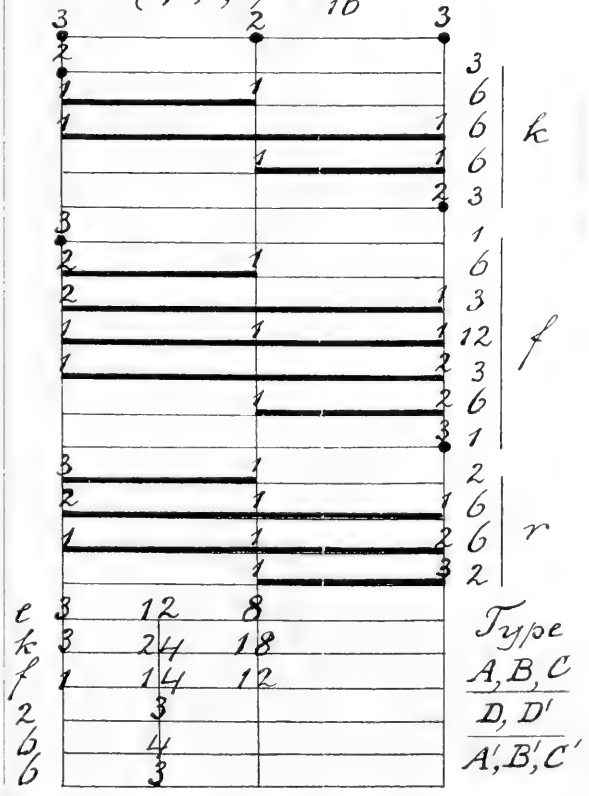
Space-fillings normal to OK_s . — Here the problem of the determination of the section of the net (C_s) loses one dimension only; so the consideration of the section of a threedimensional net of cubes by a plane normal to a diagonal shows that three sections always go together whose characteristic fractions differ by $\frac{1}{3}$ from one another. Moreover we have still to bear in mind two things. First we have to observe that the three sections of $C_8^{(2)}$ corresponding to the fractions a , $a + \frac{1}{3}$, $a + \frac{2}{3}$ do not always give three sections of a bodily inscribed sixteencell. If we assume for simplicity a to be situated between the limits 0 and $\frac{1}{3}$ we shall find three sections or $C_{16}^{(2\sqrt{2})}$ if a lies between $\frac{1}{12}$ and $\frac{3}{12}$, i.e. in half the possible cases. In the second place we have to remember that each of two or three sections of sixteencells occurs in two different orientations, being one another's mirror-image with respect to the middle plane of the prism, section of the bodily circumscribed $C_8^{(2)}$. If the intersecting space is normal to the line connecting the centre O of the chosen eightcell with the midpoint K_s of its edge PQ , then we have only to con-

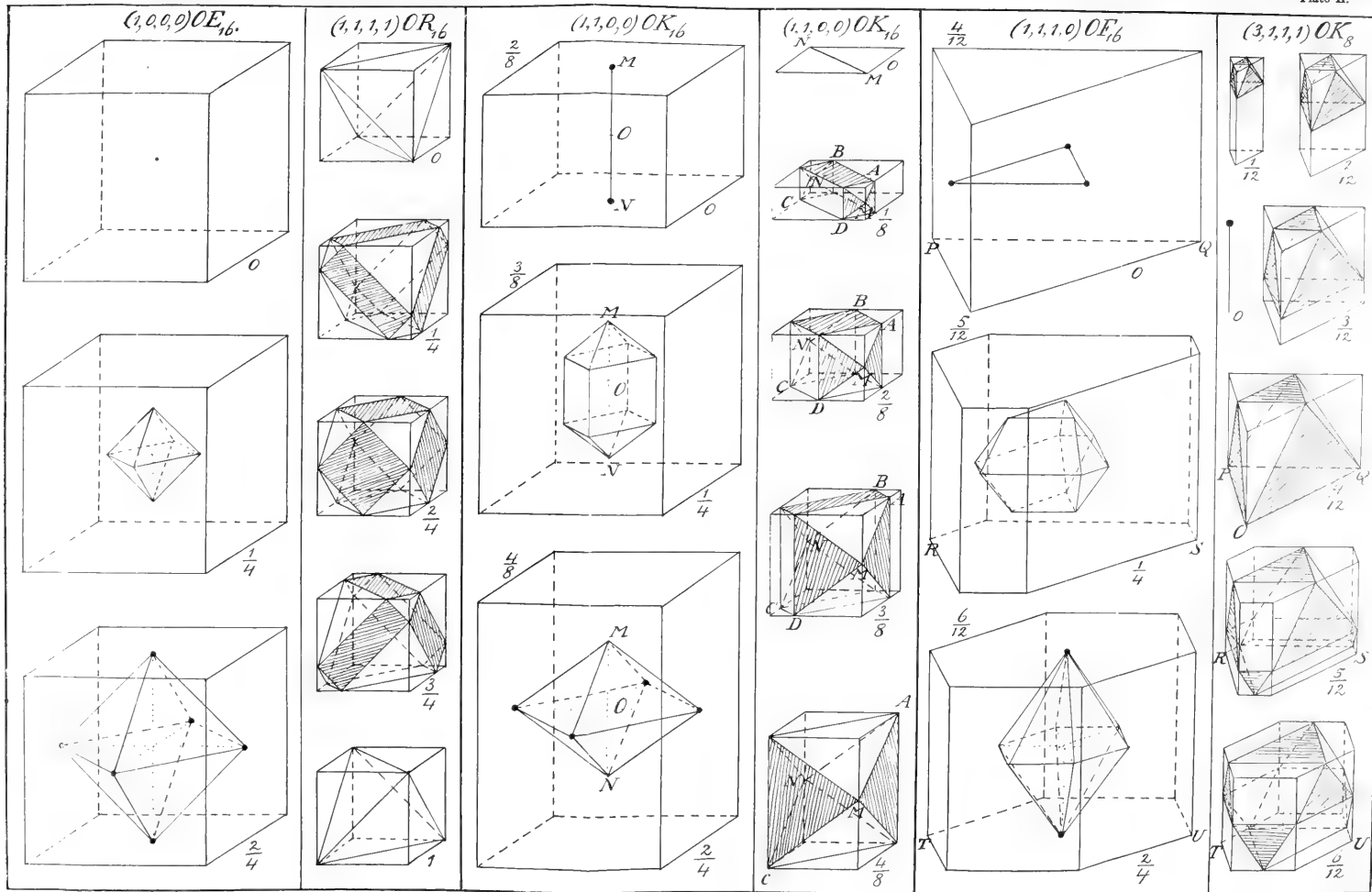
s by spaces." (Third part).

$(1,1,1,1) OR_{16}$



$(1,1,1,0) OF_{16}$





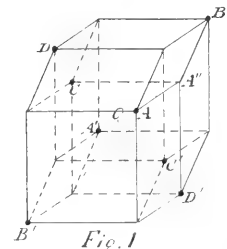


Fig. 1

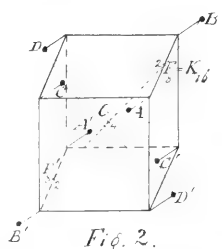


Fig. 2.

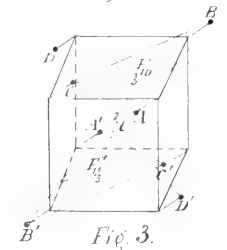


Fig. 3.

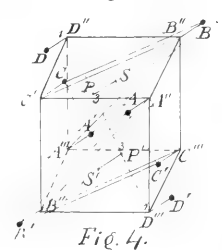


Fig. 4.

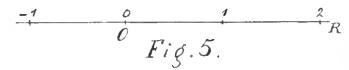


Fig. 5.

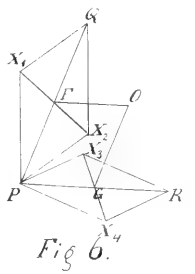


Fig. 6.

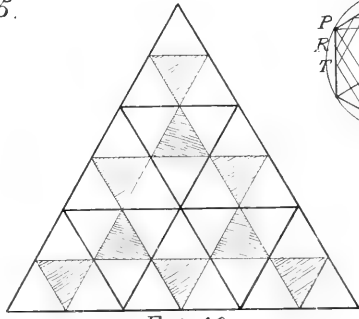


Fig. 10.

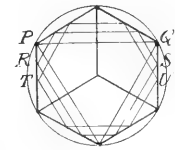


Fig. 12.

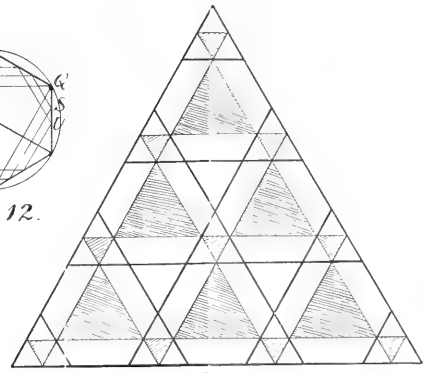


Fig. 11.

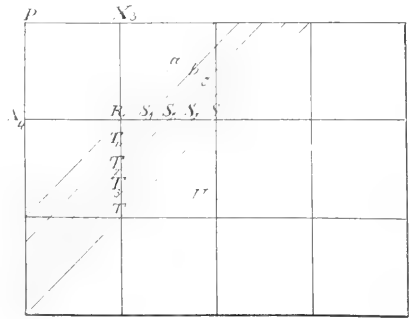


Fig. 7

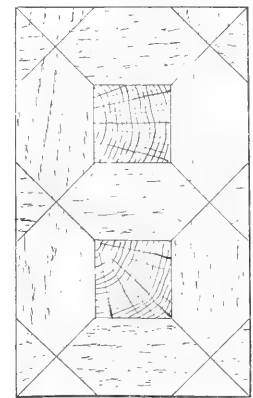


Fig. 8.^a

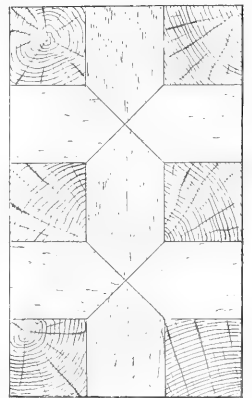


Fig. 8.^b

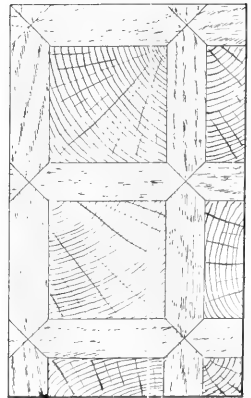


Fig. 9.^a

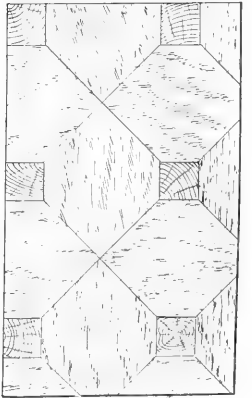


Fig. 9.^b

sider two bodily adjacent eightcells of the net, the line joining the centres of which is equipollent to PQ , in order to see that these eightcells are intersected in two congruent prisms with common base, whilst the sections with the inscribed inclined sixteencells are symmetric figures with respect to that base. If we consider difference in form only we have to deal therefore with two or three, if we also take into account difference in orientation we have to deal with four or six polyhedra.

If we deprive the problem of the intersection of the system of cells $C_8^{(4)}$ partially penetrating one another, polarly circumscribed to the erect sixteencells, of the one superfluous dimension, we find a system of cubes with edge four, the centres of which are the vertices of a net of cubes with edge two, whilst the edges are parallel to those of the cubes of the net. This system is then to be intersected by a plane normal to a diagonal. By means of a simple diagram we then find that to the three sections $a, a + \frac{1}{3}, a + \frac{2}{3}$ of the net $C_8^{(2)}$ correspond the six sections $\frac{a}{2}, \frac{a}{2} + \frac{1}{6}, \dots, \frac{a}{2} + \frac{5}{6}$ of the system $C_8^{(4)}$. But of these six different sections of $C_8^{(4)}$ only two give rise to sections of erect sixteencells, viz. those the fractions of which lie between $\frac{2}{6}$ and $\frac{4}{6}$. So we get as the two most regular of the space-fillings presenting themselves here the two indicated by figures in heavy type in the following scheme:

$$\begin{array}{l} \text{In } C_8^{(4)} \dots 0, \frac{1}{6}, \frac{2}{6}, \frac{\mathbf{3}}{\mathbf{6}}, \frac{4}{6}, \frac{5}{6} \quad \left| \quad \text{In } C_8^{(4)} \dots \frac{1}{12}, \frac{3}{12}, \frac{\mathbf{5}}{\mathbf{12}}, \frac{\mathbf{7}}{\mathbf{12}}, \frac{9}{12}, \frac{11}{12} \right. \\ \text{In } C_8^{(2)} \dots 0, \frac{\mathbf{1}}{\mathbf{3}}, \frac{\mathbf{2}}{\mathbf{3}} \quad \left| \quad \text{In } C_8^{(2)} \dots \frac{\mathbf{1}}{\mathbf{6}}, \frac{\mathbf{3}}{\mathbf{6}}, \frac{\mathbf{5}}{\mathbf{6}} \right. \end{array}$$

Of these space-fillings the first consists of regular hexagonal double-pyramids (last figure of column five of plate II) and as to shape only one other form, an irregular octahedron (the octahedron of the sixth column with OPQ as base), whilst the second one is built up by three different bodies in that supposition. The diagrams 10 and 11 represent a projection of both on the base of the prisms forming the sections of the including eightcells.

From fig. 12, added partly to fill the page, which shows the sections of a cube by planes normal to an interior diagonal, can be deduced finally that the segments of lines PQ, RS, TU of the three figures of column five — and of the last three figures of column six — of plate II have the same length.

Physics. — “*On plaitpoint temperatures of the system water-phenol*”.

By A. KEESING. (Communicated by Prof. J. D. VAN DER WAALS).

According to observations by LEHFELDT, v. D. LEE, and SCHREINEMAKERS the system water-phenol possesses maximum pressure at low temperatures. So theoretically a minimum critical temperature was to be expected, but as water shows abnormal deviations in other respects, an elaborate investigation was desirable. In view of the high critical temperatures of the components (water $365^{\circ},0$ according to CAILLETET and COLARDEAU, or $364^{\circ},3$ according to BATTELLI; phenol $419^{\circ},2$ according to RADICE) and the impossibility of using glass test-tubes (glass dissolves in water at such a high temperature) a conclusive investigation had not yet taken place as far as is known. Experimenting in a way similar to that indicated by SCHAMHARDT¹⁾ I have succeeded in arriving at a preliminary result.

As for the determination of the plaitpoint temperature there was no need for me to regulate either the pressure or the volume I did not want a CAILLETET tube, but used small closed test-tubes of *quartz*. This made it possible for me to use a vapour-jacket whose bottom was also glass, and which rested on asbestic iron gauze. In consequence of this one of the two nickelin wires, viz. the one used by SCHAMHARDT to heat his boiling-liquid, could be dispensed with, and replaced by a BUXSEX burner. The second wire, which enabled him to prevent satisfactorily the radiation at temperatures between 200° and 300° , proved insufficient for temperatures between 350° and 400° . A second layer of asbestos round the wire gave some improvement, but the radiation appeared to be completely prevented only when I placed a glass cylindre silvered on the inside, in which two slits were left free for reading, round the vapour-jacket, which had been thus wrapped up. This cylindre of a diameter 5 centimeters larger than that of the jacket, was shut off by means of asbestos wool on the upper and the lower side.

It was not without difficulty that we found a boiling-liquid, for in the Phys. Chem. tables of LANDOLT-BÖRNSTEIN no boiling-liquids are given above 360° . I used *benzidine*, an inactive substance, which boils at 1 atm. pressure at $\pm 400^{\circ}$ with colourless vapour. We have, however, to bear in mind:

1. that chemically pure benzidine be used, because impure benzidine boils irregularly, and covers the vapour-jacket, the quartz tube, and the thermometer with a tough, tarry layer, which prevents

¹⁾ H. C. SCHAMHARDT. Isotherms of mixtures of benzene and aether. Thesis for the doctorate p. 12—16.

the observation and which I could only remove partially by boiling long with water and benzene,

2. that the substance be boiled under nitrogen, as pure benzidine is soon contaminated by the oxygen from the air,

3. that superheating, which causes the liquid benzidine at times to rise $1\frac{1}{2}$ decimeter in the jacket, be prevented by a good quantity of glass-wool.

When benzidine was used, a cooler was not wanted, the vapour condensing in the narrowed part of the vapour-jacket.

The benzidine being heated under nitrogen, I required a nitrogen reservoir. For this purpose a 100 L. flask was used, which was filled with nitrogen obtained from a saturate solution of equal units of weight of potassium nitrite and ammonium chloride. When the reservoir had once been filled, the nitrogen could be expelled from the flask by the admission of water, and be conducted through a drying apparatus to the vapour-jacket. The pressure in the reservoir was measured by a manometer.

The experiments proper began with the filling of the nitrogen reservoir. The phenol and water were weighed in the required ratio, and heated with a spirit lamp. The temperatures at which water and phenol do not mix appeared then to be exceeded, and a homogeneous liquid was formed. A thick-walled quartz tube closed on one side, and drawn out capillary on the other side in the voltaic arc was now heated in the free flame, and the air expelled under the phenol water solution; the liquid now rose in the tube which was filled for more than $\frac{1}{3}$, and then fused together in the voltaic arc. The quartz appeared then to be a very suitable material. It is as clear and transparent as glass, but, when hot, may be cooled in cold water without bursting; it may be heated in a free flame, and is proof to high pressures, as the critical pressure of water, viz. 200 atm. Protective measures proved to have been most likely superfluous.

Thermometer and quartz tube were fastened by means of copper wires in a hole of the glass tube which pierces the airtight rubber stopper of the vapour-jacket. The apparatus were filled with nitrogen, the pressure in the boiling vessel was reduced to about 30 cm., the gas-burner lighted, and every five minutes a lamp was inserted of the resistance, by the aid of which the current required to check radiation was regulated. After an hour the thermometer indicated about 350° . As soon as this temperature had become constant, which also appeared from the fact that the boiling phenomena stopped in the

quartz tube, nitrogen was gradually admitted. The meniscus began then to become gradually fainter. The incandescent lamps placed behind the slit made the inner wall of the quartz tube look like a streak of light, in which the meniscus made a notch. By moving the eye to and fro in front of this notch I could ascertain the presence of the liquid mirror as long as possible. The temperature at which the meniscus disappeared, was noted down; also the temperature at which the liquid mirror returned on decrease of pressure in the vapour-jacket.

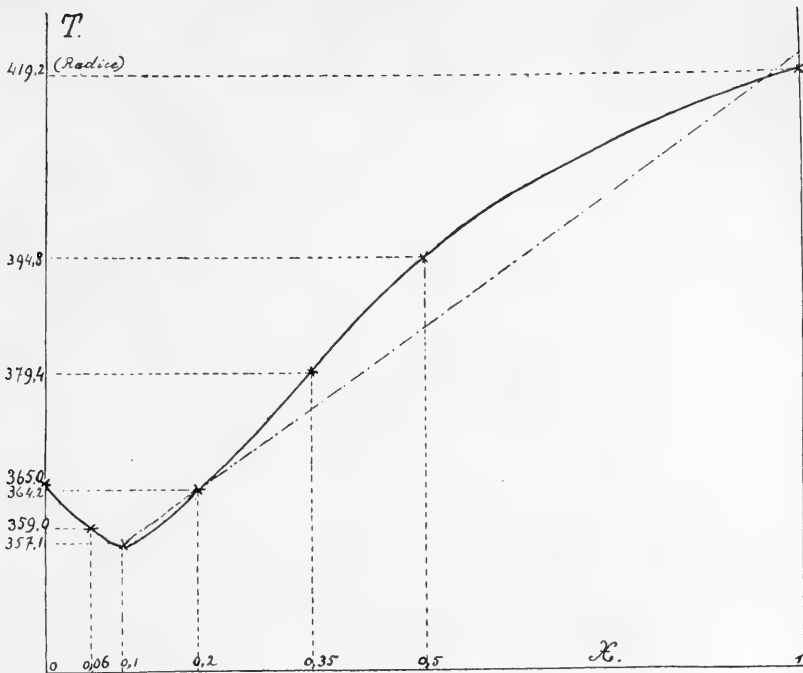
First the T_k of the mixture $x = 0,1$ was determined; compared with CAILLETET and COLARDEAU'S observations this gave a *decrease* of 8° in the critical temperature. So there was no doubt but a minimum of temperature was present in the plaitpoint-line.

To see whether the decrease would continue, $x = 0,2$ was determined; we found $\pm 364^\circ$; the T_k , though rising, was still below the value given by CAILLETET and COLARDEAU for $x = 0$. In order to determine the place of the minimum more accurately, the first component ($x = 0$) and the mixture $x = 0,06$ were then examined; finally also $x = 0,5$ and $x = 0,35$ with a view to the course of the plaitpoint line beyond the minimum.

The observations have been put together in the subjoined table; they have been reduced on a thermometer tested at the Reichsanstalt, which does not show any deviation at 300° , but points one degree too low at 400° .

x	The meniscus disappeared at	The meniscus returned at	The meniscus disappeared for the second time at	The meniscus returned again at
0	365.0	363.9	365.0	364.2
0.06	359.0	358.5	359.0	358.4
0.1	357.0	356.0	357.1	356.0
0.2	364.2	363.0	364.1	363.3
0.35	379.4	378.0	379.3	378.0
0.5	394.8	393.8	394.8	393.9
1	419.2 according to Radice			

Graphically represented we obtain the following T/x -projection of the plaitpoint line:



From this graphical representation follows :

1. that the system water-phenol really possesses a *minimum* plait-point temperature,

2. that it lies in the neighbourhood of $x = 0,1$. Now SCHREINEMAKERS has found that the mixture $x = 0,011$ has maximum pressure at 56° , the mixture $x = 0,015$ at 75° , and $x = 0,017$ at 90° . These observations deviate from the theory, for the maximum pressure point does not move to the right with higher temperature, but to the left. If, however, we choose one of SCHREINEMAKERS' observations, no matter which, then the fact that the minimum plaitpoint temperature lies at an x larger than that of the mixtures for which maximum pressure is still possible, is in accordance with the theory.

3. As the extremities of the ordinates belonging to the abscissae $x = 0,1$, $x = 0,2$, and $x = 1$ lie about on a straight line, and as those belonging to $x = 0,35$ and $x = 0,5$ are obviously above it, we must conclude to the presence of a *point of inflection* in the Tx projection of the plaitpoint curve. It is doubtful whether we must attach physical significance to this.

In conclusion I have still to mention that in these observations no electro-magnetic stirring-apparatus has been used, which, however, may be applied as soon as a quartz stirrer of sufficiently small diameter is ready.

Amsterdam, *Physical Laboratory.*

Petrography. — “*The mineralogic and chemical composition of some rocks from Central Borneo*”. By J. SCHMETZER. (Communicated by Prof. A. WICHMANN).¹⁾

(Communicated in the meeting, of October 31, 1908).

Prof. M. DITTRICH at Heidelberg analyzed the following four rocks, collected by Prof. G. A. F. MOLENGRAAFF in Central Borneo :

- II 710, a glassy amphiboledacite, found as a boulder on a boulder-bank in the Soengei Sebilit, \pm 3 KM. above Kebijau.²⁾
- II 599, the glassy amphiboledacite of which consist the rocks, 1.50 m. high, in the Soengei Embahoe, below Nangah Pämali; the hand-specimen was struck close to the contact with the adjacent rock (silicific tuffbreccia).³⁾
- II 749, biotiteamphiboleandesite with old habitus from the right bank of the Soengei Tebaoceng over against Nangah Oeroei.⁴⁾
- I 893, aplitic microgranite from the waterfall, N.W. cliff, Boekit Këlam.⁵⁾

I. *Hyalopilitic Amphiboledacite* (Amphibolephyrivitroyellowstonose).

The grey-black, glassy rock shows a rough, conchoidal fracture; only very indistinctly a few white feldspar-phenocrysts, whose diameter does not exceed 1 mm., and very rare, bright glittering, still smaller green amphibole-needles appear forth from the greasy-shining ground-mass. Under the microscope the *plagioclase* of the first generation (andesine-oligoclase) forms sharp idiomorphic crystals, lying mostly isolated, but sometimes combining into aggregates. Zonal structure is locally finely developed; among the twin-laws the albite-law reigns, the Carlsbad- and pericline-law occur only subordinately. Here and there the feldspar shows a pronounced inclination to forming skeleton

¹⁾ The Dutch communication was entitled “The mineralogic and chemical composition of some rocks from the Müller-Mountains in Central-Borneo”. I avail myself of this opportunity to repair a lapsus calami, only the three first rocks described originating from the Müller-Mountains, Mt. Këlam not forming part of this range.

²⁾ cf. MOLENGRAAFF, Geological Explorations in Central Borneo, Leyden 1902, 209, where this rock is named pitchstone.

³⁾ The label bears the indication “ $\frac{1}{4}$ Km. below Nangah Pämali”, whilst according to MOLENGRAAFF’s description, op. cit. 267, and the map VIIIb, published by him at the same time, this should rather be about 100 meters. There can be no doubt, however, about the identity of the rock meant by him in his work i.e., with that described here, as the rock builds up the *first* dyke of andesite in the tuffbreccia below Nangah Pämali.

⁴⁾ Mt. Loeboek consists of the same rock, *ibid.* 293 - 295.

⁵⁾ *ibid.* 127 (Chapt. VI), 138.

crystals, partly in consequence of differences in the velocity of crystallization in not equivalent directions, by which planes (by preference (010)) broaden lamellarly to far beyond the original boundary ribs, partly by a dense accumulation of glass-inclusions with negative crystal-forms, which at bottom is connected with the same phenomenon. These glass-inclusions press the feldspar-substance together into narrow little laths with two main directions and which combine into a very complicated meandrous pattern, while also the crystal-circumference assumes an irregular indented shape. The glass, however, also forms irregular notch-like or claviform inclusions and is neither in colour, nor in the nature of the microlites to be distinguished from the glass of the groundmass.

The *amphibole* occurs in fresh little columns and crystal-fragments; the corrosion of the crystals by the magma at the effusion has not given rise to the origin of a proper resorption-border, but has confined itself to rounding the crystals and largely accumulating the magnetite-globulites of the groundmass along their periphery. The dichroism moves between darkgrey-green // the *c*-axis and greenish grey-yellow perpendicularly here to; with regard to the axis of elongation an extinction of 15° was measured. Parallel to (100) and (001) we sometimes find a narrow twin-lamella linked between. Besides the good prismatic cleavage a system of rough cracks shows itself perpendicularly to the *c*-axis. Quartz is wanting.

The *groundmass* consists principally of colourless glass in which excellent idiomorphic lathshaped or tabular feldspars, the former often with fine skeleton-forms and exhibiting a fluidal texture, come to the front. Albite-lamellae and feeble zonal structure are general, glass-inclusions much less frequent than in the phenocrysts; on the other hand the crystals contain many microlites of magnetite and bronzite. Those two last minerals take an important place among the secretions of the base. The magnetite, which on the ground of the chemical analysis seems to contain TiO_2 , may, according to the size, be brought to two distinctly separated generations. The intratelluric magnetite (average crystal diameter 15μ) forms excellent octahedrons, which occur both in the groundmass and in the phenocrysts. In the groundmass the magnetite crystals are found partly isolated, partly in aggregates and then often grown together to dendritic markings. That the on an average $10 \times$ smaller magnetite-crystals and globulites, occurring by the side of those mentioned above, did not crystallize until the effusion-period, is proved by their accumulation at the circumference of the corroded amphibole-substance. The *bronzite* forms a pretty compact tissue of slender needles, which generally show an

irregular transverse cracking. From the feldspar-microlites they are distinguished by the strong refraction, from apatite (occurring as inclusion in the plagioclase-phenocrysts) by their behaviour when tested it by means of a $\frac{1}{4} \lambda$ mica plate in parallel polarized light, from the very few dichroitic, green, sometimes parallel to a (100) twinned hornblende-prisms of the second generation, mixed up with them, by the very light colour, the weak double refraction and the right extinction.

The grounds on which the presence of bronzite, and not of enstatite or hypersthene is assumed, will further be explained. We can conclude the microscopic description by mentioning the occurrence of extremely fine undefinable microlites with a strong double refraction, whose length is only a few $\mu\mu$, the width by estimate no more than 0.1 μ .

The chemical analysis yielded the following values, from which is calculated the norm of the rock according to CROSS, IDDINGS, PERSSON and WASHINGTON ¹⁾.

	%	Mol. Prop.	ilm.	orth.	alb.	anorth.	cor.	magn.	bronz.	quartz
SiO ₂	66.16	4.103	—	126	384	124	—	—	33	436
Al ₂ O ₃	15.39	0.451	—	21	64	62	4	—	—	—
Fe ₂ O ₃	1.25	0.08	—	—	—	—	—	8	—	—
FeO	1.72	0.024	6	—	—	—	—	8	10	—
MgO	0.90	0.023	—	—	—	—	—	—	23	—
CaO	3.47	0.062	—	—	—	62	—	—	—	—
Na ₂ O	3.94	0.064	—	—	64	—	—	—	—	—
K ₂ O	2.00	0.021	—	21	—	—	—	—	—	—
H ₂ O ¹⁾	4.94	—	—	—	—	—	—	—	—	—
TiO ₂	0.50	0.006	6	—	—	—	—	—	—	—
	100.27									

¹⁾ Loss of ignition 5.11 %.

¹⁾ Quantitative classification of Igneous Rocks, Chicago, 1903.

From this the following norm may be calculated:

quartz	26.16	$Q = 26.16$	}	Sal = 89.03
orthoclase	11.68	$F = 62.46$		
albite	33.54			
anorthite	17.24			
corundum	0.41	$C = 0.41$	}	Fem = 6.39
bronzite	3.62	$P = 3.62$		
magnetite	1.86	$M = 2.77$		
ilmenite	0.91			

so that according to the American system the rock belongs to Class 1 (Persalane); Subclass 1, (Persalane); order 4 (Brittanare); Rank 3 (Coloradase); Subrank 4 (Yellowstonose). The only positive deviation, which the mode shows with respect to the norm, is the presence of amphibole, so that the described rock ought to have the name of Amphibolephyrivitroyellowstonose¹⁾.

The chemical analysis throws some light on the nature of the rhombic pyroxene. The microscopic examination stopped at the observation that the pyroxene was distinguished from the hypersthene by its light colour. The above combination of the oxydes to mineral-molecules now proves that in the pyroxene-molecule MgO predominates strongly with respect to FeO. That the mode of the rock by the appearance of amphibole deviates somewhat from the norm calculated here, does not alter this fact considerably; even if we set aside the circumstance, that the amphibole is quantitatively far inferior to the crystalized rhombic pyroxene. For the fact that in the resorption of the amphibole-phenocrysts only magnetite, no pyroxene as a new

¹⁾ In spite of the lack of quartz in this rock, it is, on the ground of the high SiO₂ quantity, ranked not under the andesite but under the dacite; the same thing was done with the rock II 599 from the Soengei Embahoe. With the rock-analyses, gathered by OSANN, Beiträge zur chemischen Petrographie, II Teil, Stuttgart 1905, the above types are grouped as follows after the SiO₂ quantity (not free from H₂O):

SiO ₂ in %	75	74	73	72	71	70	69	68	67	66	65	64	63	62	61	60	59	58	57	56	55	54	53	52	51	50
Nr. of analyses	}	Dacite		1	—	1	—	3	5	4	7	3	4	3	3	2	1	1	—	—	—	—	—	—	—	—
		Andesite		—	—	—	—	1	2	1	10	6	10	9	11	20	24	16	13	10	16	12	6	2	3	3

From this may be calculated that the SiO₂ quantity with the dacite is fluctuating round a mean of 67.5%, with the andesite round 59.5%. Of course these figures have only a very relative value; the rocks II 710 and II 599 however take up places also in the projection-triangle of OSANN which fall entirely within the sphere of the dacite- and quartzporphyriteprojections, but only near the border of the sphere of the andesites (glimmer-, hornblende-, hypersthene resp. augiteandesites and porphyrites, cf. OSANN, Versuch einer chem. Classification der Eruptivgesteine, Tsch. Min. Petr. Mitt. XX, Heft 5. 6 1900, Taf. IX, X).

secretion shows itself, justifies the supposition that the amphibole must be said to belong to the ferruginous varieties, and from this may be concluded that the ratio of the oxyde-quanta MgO and FeO, which after the crystallization of the amphibole remained available for the formation of rhombic pyroxene, could not be altered very much at the expense of MgO, compared with the ratio which the norm-calculation yields. These different grounds, therefore, tell against hypersthene, and for bronzite or ferruginous enstatite. In accordance with our conclusion, as will appear further on, unmistakable enstatite-(bronzite-)crystals of greater dimensions are found in the glassy dacite II 599 of the Soengei Embahoe, which has a close chemical and mineralogic similarity with this rock. There, too, the glass-base possesses the same characteristic rhombic pyroxene microlites, whose bronzite-nature is made probable by the chemical analysis.

Fe₂O₃ being reduced to FeO, the molecular proportions, calculated on a sum of 100, yield the following values (TiO₂ added to SiO₂):

SiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O
75.45	10.27	2.72	1.56	4.22	4.35	1.43

from which follows the formula according to OSANN:

	s	A	C	F	a	c	f	n	m	k	Series
I	75.45	5.78	4.49	4.02	8.09	6.28	5.62	7.53	10.00	1.46	a v
II	75.45	5.78	4.22	4.29	8.09	5.90	6.00	—	—	—	
III	—	—	—	—	(12.14	9.42	8.43)	—	—	—	
IV	—	—	—	—	(12.14	8.85	9.00)	—	—	—	

These figures require some explanation. As appeared already at the calculation of the norm, there remained after saturation of the alkalis and CaO with Al₂O₃ a not unimportant quantity of sesquioxide. The analyzed material being absolutely fresh and even microscopically free from every trace of decomposition, there is no possibility of a relative increase of Al₂O₃ by a removal of alkalis and CaO: a consequent distribution of the Al₂O₃-remainder over alkalis and CaO¹⁾ could not be reasonably defended here. Also the dissolution by the andesite-magma of fragments from an adjacent rock rich in aluminium cannot but be highly improbable; both macroscopically and microscopically there is not the least indication for it. For the rest the Al₂O₃-remainder cannot be found in amphiboles or pyroxenes²⁾

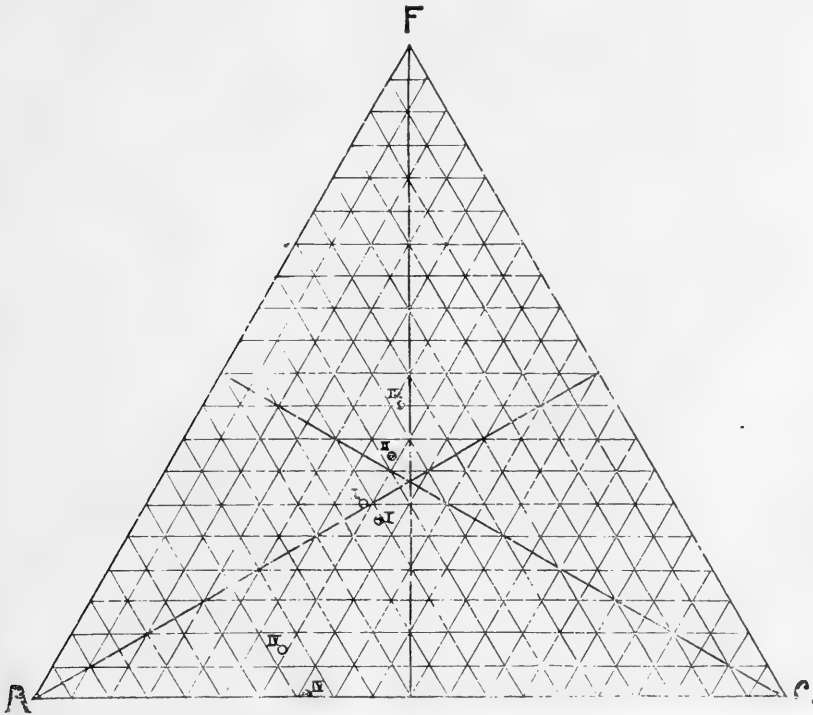
1) L. MILCH, Ueber Spaltungsvorgänge in granitischen Magmen nach Beobachtungen im Granit des Riesengebirges, Festschrift H. ROSENBUSCH, 1906, 127.

2) A. OSANN, Versuch einer chemischen Classification der Eruptivgesteine, Min Petr. Mitt. XXII, 1903, 337.

exceedingly rich in Al_2O_3 , as appears sufficiently from the microscopic examination; it has on the contrary to be looked for in the glass of the groundmass.

In the rare cases, in which after saturation of the alkalis and lime an Al_2O_3 -remainder shows itself, OSANN substitutes MgO in the atom-group (CaAl_2O_4 ¹⁾), whilst BECKE ²⁾ neglects the Al_2O_3 -rest in the formula and mentions it separately; it amounts here in molecular proportions to 0.27. Accordingly in I the rock-formula is given according to OSANN, in II after BECKE. In III and IV these double values for a, c and f after BECKE have been calculated on a sum of 30 instead of 20 (I and II).

In the following graphic notation I denotes the projection of the rock; the filled circle with the values of a, c, f according to OSANN as base, the one not filled with those according to BECKE.



II. *Hyalopilitic Amphiboledacite* (Amphibolephyrivitroyellowstonose).

From the glassy base of this greasy-shining, blackish grey rock, which shows an inclination to a conchoidal fracture and in one of the hand-specimens a distinct and pretty regular separation into thin, level plates from 1—7 mm. in thickness, already macroscopically small plagioclases with lively microtine-habitus and glittering amphibole-prisms are coming forth. The very fresh, also here mostly idio-

¹⁾ Min. Petr. Mitt. XXII, 1903. 337.

²⁾ Ibid. 215.

morphic, prismatic and tabular *plagioclase*-phenocrysts are often lying together in groups and possess an excellent zonal structure showing itself already in obliquely transmitted ordinary light by parallel strongly luminous stripes and in which acid and basic zones frequently interchange. The same twin-laws are found as in the preceding rock; the albite-lamellae sometimes fit into each other with irregular indentations, in consequence of which through the growing together of several crystals a confused polarization-image arises. The plagioclase of the phenocrysts belongs to somewhat more basic mixtures than in the preceding dacite; the basicity falls to that of basic labrador, but on the other side approaches that of andesine. The crystallization of the basic plagioclase had already ended before that of the amphibole-phenocrysts, but for a time coincided with it; the more acid plagioclase on the other hand often contains amphibole-prisms inclosed. According to the dimensions the plagioclases in this rock may be divided into three groups: *a*) crystals with an average diameter of 1.5 mm., generally strongly laden with colourless and brown glass-inclusions and often entirely filled with these, with the exception of a peripheric zone; *b*) crystals, on an average twice as small and in which the brown glass-inclusions are very rare, the colourless ones on the whole being much less numerous; *c*. still smaller prismatic crystals, which always show a zonal structure and a twinning after the albite- and Carlsbad-law, and which gradually pass into the youngest and smallest skeleton-shaped, mostly fluidally arranged feldspars of the glass-base. Whilst *b* has still to be reckoned among the real phenocrysts, *c* had better be placed in the second generation. As appears, the boundary-line between the crystals of the 1st and 2nd generation can with the feldspars not be drawn exactly, though there is no doubt about the extremes. Higher up we mentioned the appearance of two kinds of glass-inclusions, which also here often assume the form of negative crystals: 1. of almost colourless ones, which seem to have a very light pink tinge and sometimes contain numerous microlites and 2. of brownish grey ones, which are strongly spherulitically devitrified. The nature of this brown glass, also occurring in patches in the colourless glass-base, is not quite obvious. Only it seems to be certain that the brown glass has no genetic relation with the colourless. But then these two sorts of glass must have existed side by side as far back as the intratelluric period, as they occur by the side of each other in the plagioclase and amphibole phenocrysts. Therefore the brown glass probably contains dissolved foreign matter, or, what is perhaps more acceptable, it is a product of intratelluric liquation.

The *amphibole*, which abundantly occurs, forms blunt needles, not exceeding a length of 1 mm. : c = green, b = greyish green and a = greyish yellow, in which $c > b > a$, but c and b differ only insignificantly. Now and then a zonal structure comes to the front, which is perceptible especially in some sections perpendicular to the axis of elongation. In this case there is seen parallel to the crystal-circumference a zone, showing the colours a = blue greyish green or dark greyish green, b = brown greyish green, c = light greyish green. The idiomorphic crystals have often been so strongly affected by resorption, that the groundmass penetrates into them with deep windings. The resorption-border is formed by an exceedingly dense felt-like tissue of fine microlites, becoming larger here and there, in some places even exceeding the feldspar-laths of the groundmass in size and which can then with certainty be recognised as a rhombic pyroxene. Mixed with them we find magnetite and strongly double-refracting grains, which have probably to be taken for augite. The resorption-border is not everywhere distinctly developed, in some crystals it seems even to be wanting partially. An explanation of this might be given by the supposition that the rock, even after the resorption-period, has been raised with violence, by which movement the components of the resorption-border were in some places swept away from the phenocryst. This conception is positively backed by the observation that the border often passes cloudlike into the groundmass, while the bigger needles pretty generally by transversal cracks are broken into pieces, which have lost their mutual orientation. But besides the components of the first generation show mechanical deformations, which have come about before the solidification of the glass-base and in all probability after the resorption-period. The feldspar shows irregular fissures and rents, along which pieces of broken twin-lamellae have sometimes moved with respect to each other and which are filled with glass of the groundmass as soon as the fragments through a mutual transposition are no longer closely united.

By irregular cracks perpendicular to the axis of elongation, the amphibole too is nearly always broken into fragments, which are often tolerably far carried away from each other; not rarely also opened wide along the cleavage directions. Also here the gaping rents are filled with glass and stress is to be laid upon the fact that this glass is nearly always entirely free from the resorption-products, which show themselves along the original crystal-boundaries. This proves that those rents were opened at an epoch when the resorption-period was all but over, a conclusion which is wholly in accordance with the above fact that the needles themselves, forming the

From which follows the following norm :

quartz	25.38	Q = 25.38	}	Sal = 86.58
orthoclase	6.67	F = 61.20		
albite	35.63			
anorthite	18.90	}	Fem = 9.03	
diopside	1.54			P = 6.03
bronzite	4.49			
ilmenite	0.91	M = 3.00	}	
magnetite	2.09			

and the rock is placed in Class I (Persalane); Subclass 1 (Persalane); Order 4 (Brittanare); Rank 3 (Coloradase); Subrank 4 (Yellowstonose).

If we take into consideration that the diopside-molecule is crystallized as amphibole, there is a satisfactory agreement to be observed between norm and mode.

If Fe_2O_3 is reduced to FeO , the molecular proportions, calculated on a sum of 100 (TiO_2 added to SiO_2) give the following values:

SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O
74.14	9.97	2.83	2.63	5.05	4.58	0.81

so that the formula according to OsANN is:

	s	A	C	F	a	c	f	n	m	k	Series
I	74.14	5.39	4.58	5.93	6.78	5.76	7.46	8.5	9.2	1.56	av
II	(10.17 8.64 11.19)										

In I $a + c + f = 20$; in II $a + c + f = 30$.

Both dacites, therefore, show a great chemical similarity, which is also expressed by the graphic notation, fig. 1. The somewhat greater basicity of the second rock, which contains more CaO and MgO , a little less SiO_2 , and half the quantity of K_2O , manifests under the microscope by the character of the feldspars and the greater quantity of amphibole.

In order to compare them some analyses have been brought together, which show a great similarity with the two discussed above:

	I	II	III	IV	V	VI	VII
SiO ₂	67.34	66.16	65.88	65.72	65.66	65.39	64.81
Al ₂ O ₃	15.96	15.39	15.61	15.06	15.61	15.49	15.73
Fe ₂ O ₃	3.38	1.25	2.42	1.35	2.40	2.80	1.68
FeO	0.80	1.72	2.71	1.80	2.07	1.99	2.91
MgO	0.88	0.90	1.76	1.57	2.46	2.06	2.82
CaO	2.98	3.47	3.70	4.18	3.64	4.48	4.22
Na ₂ O	4.12	3.94	3.92	4.24	3.65	4.56	3.98
K ₂ O	1.66	2.00	2.29	1.07	2.03	1.59	1.43
H ₂ O+	2.20	4.94	1.05	3.77	1.07	0.55	0.62
H ₂ O-	—	—	—	0.69	—	—	—
CO ₂	—	—	sp.	—	—	—	—
TiO ₂	0.56	0.50	0.43	0.48	1.37	—	0.08
P ₂ O ₅	—	—	0.13	—	sp.	0.11	0.23
MnO	—	—	0.08	—	—	—	0.08
Sum	99.78	100.27	100.00	99.93	100.27	99.02	100.61

- I. Biotitedacite, Kolantziki, Megara, Greece, anal. A. RÖHRIG, cf. WASHINGTON, Journ. Geol. III, 150, 1895 (Yellowstonose).
- II. Amphiboledacite, boulder from boulder-bank, S bilit-river, ±3 KM. above Këbijau, anal. M. DITTRICH.
- III. Granitite, Mazaruni District, Brit. Guyana, anal. J. B. HARRISON, cf. WASHINGTON, Chem. Anal. of Igneous Rocks, 1903, 191 (Yellowstonose).
- IV. Amphiboledacite, first dyke below N^a Pëmalì, Embahoe-river, anal. M. DITTRICH.
- V. Dacite, Sepulchre Mountain, Yellowstone nat. Park, anal. J. E. WHITFIELD, cf. J. P. IDINGS, XII Ann. Rep. U. S. Geol. Surv. I, 648, 1891 (Yellowstonose).
- VI. Pyroxenedacite (Quartzpyroxeneandesite), Cumbal, Columb. Andes, cf. KÜCH, N. Jahrb. f. Min. 1886, I.
- VII. Biotiteporphyrite, North Mosquito, Col., anal. HILLEBRAND, cf. CROSS, XII^A Monogr. U. S. Geol. Surv., CLARKE, U. S. Bull. No. 168, 155. (Yellowstonose).

III. *Biotiteamphiboleandesite* (Biotiteamphibolephyrovitritonalose).

The rock of which Boekit Loeboek is composed, and of which the handspecimen II 749, struck over against Nangah Oeroei on the Soengei Tebaoeng, represents a sample, belongs to the freshest old andesites of the Western Müller-mountains. After the macroscopic habitus it takes a place quite by itself; a darkgreen groundmass, strongly fading in the more weathered rock, forms the cement between irregularly scattered plagioclases with microtine-habitus, sometimes densely crowded together and reaching a diameter of 6 mm., slender amphibole-crystals (to 8×2 mm.) and hexagonal little tables of bronze-coloured biotite (3–4 mm. diam.). The twinned, often very distinctly zonal *plagioclase* is not really different from the one described above. The very first beginning of decomposition shows itself in a slight development of albite, secondary amphibole and troubling substances along cracks. The plagioclase, for the rest limpid, contains as inclusions primary amphibole, often twinned parallel to (100), magnetite, apatite, and occasional sharp prisms of zircon, whilst peripherically sometimes augite-grains are inclosed, which are characteristic of the resorption-borders of the amphibole-phenocrysts, and from this appears that the crystallization of the plagioclase did not come to an end until during or after the eruption.

The *amphibole* forms prismatic individuals, which are strongly corroded by the magma and surrounded by a broad, loose border of chloritizing amphibole-scales, pyroxene-, magnetite- and titanite-grains, mixed with the usual groundmass-components. Slender prisms are sometimes, to within a narrow, notched lath, entirely changed into these products. The extinction with respect to the *c*-axis reaches a value of 20° ; the pleochroism varies between dead brownish green and light brownish green; the usual twins parallel to (100) occur. As for inclusions the amphibole contains basic plagioclase, magnetite and cloudlike accumulations of extremely fine, parallel microlites, which probably, quite like a part of the magnetite-globulites, owe their individualisation to a chemical dissociation of the amphibole substance. The examination of the *biotite* yields no particular points of view. The acid *groundmass* consists of probably primary grains of quartz with wavy extinction containing colourless limpid glass-inclusions, sanidine and acid, short prismatic and zonal, but also slender lath-shaped plagioclase with polysynthetic twinning after the albite-law; these minerals are cemented by a small amount of colourless glass, strongly troubled by globulites. Here and there some grains of almost colourless augite, sometimes twinned and strongly laden with glass, are found, which as appears from their occurrence near the

resorption-zones of the amphibole-phenocrysts, even there, where they assume more considerable dimensions (to 0.1 mm.), must be considered as resorption-products. The glass of the groundmass contains magnetite in octahedrons, grains and prisms of apatite and of zircon, and is everywhere pushed away by fibres and little scales of a green chloritic product, strongly accumulating round the amphibole-phenocrysts and having formed principally at the cost of the secondary amphibole secreted in the resorption.

The analysis of the freshest material gave the following results :

	%	Mol. Prop.	ilm.	magn.	ham.	orth.	alb.	anorth.	diops.	enstat.	quartz
SiO ₂	62.70	1.045	—	—	—	114	396	152	22	52	309
Al ₂ O ₃	16.37	0.161	—	—	—	19	66	76	—	—	—
F ₂ O ₃	2.81	0.018	—	14	4	—	—	—	—	—	—
FeO	1.62	0.022	8	14	—	—	—	—	—	—	—
MgO	2.50	0.063	—	—	—	—	—	—	11	52	—
CaO	4.84	0.087	—	—	—	—	—	76	11	—	—
Na ₂ O	4.05	0.066	—	—	—	—	66	—	—	—	—
K ₂ O	1.83	0.019	—	—	—	19	—	—	—	—	—
H ₂ O—105°	0.87	—	—	—	—	—	—	—	—	—	—
HO +105°	1.79	—	—	—	—	—	—	—	—	—	—
TiO ₂	0.64	0.008	8	—	—	—	—	—	—	—	—
	100.02										

from which follows the composition :

Quartz	18.54	Q = 18.54	} Sal = 84.81
orthoclase	10.56	} F = 66.27	
albite	34.58		
anorthite	21.13		
diopside	2.38		} P = 7.58
enstatite	5.20		
ilmenite	1.22	} M = 5.11	
magnetite	3.25		
haematite	0.64		

The rock therefore belongs to Class II (Dosalane); Subclass I (Dosalone); Order 4 (Austrare); Rank 3 (Tonalase); Subrank 4 (Tonalose). The greater basicity with respect to the above mentioned rocks shows itself chemically in the decrease of the SiO₂, the increase

of the MgO and the CaO quantity. The mode deviates rather considerably from the norm by the presence of biotite and amphibole, which minerals have to be considered as the bearers of the MgO, which is put here under the enstatite-molecule. A portion of the MgO, however, also occurs in the augite and the amphibole of the resorption-border and in the chlorite.

The molecular proportions calculated on a sum of 100 — Fe₂O₃ reduced to FeO — yield:

SiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂
69.34	10.68	3.85	4.18	5.77	4.38	1.26	0.53

Formula according to OSANN:

s	A	C	F	a	e	f	n	m	k	Series
69.87	5.64	5.05	8.75	5.8	5.2	9	7.7	9.2	1.33	<i>av</i>
			(8.7)	(7.8)	(13.5)					

In the graphic notation it is the basic character which, by the side of the close similarity between the two preceding dacites, is distinctly expressed. To make a comparison we give here the analyses of some chemically closely allied rocks:

	I	II	III	IV	V	VI
SiO ₂	62.78	62.70	62.27	62.09	62.09	61.22
Al ₂ O ₃	17.16	16.37	16.92	17.03	16.69	16.14
Fe ₂ O ₃	1.96	2.81	2.40	2.38	1.45	3.01
FeO	2.31	1.62	2.59	2.69	3.76	2.58
MgO	2.32	2.50	2.87	3.08	1.93	4.21
CaO	4.84	4.84	4.78	5.65	6.08	5.46
Na ₂ O	4.11	4.05	4.72	4.10	3.36	4.48
K ₂ O	2.15	1.83	1.47	1.67	1.84	1.87
H ₂ O+	0.88	1.79	1.22	0.13	1.47	0.40
H ₂ O—	0.24	0.87	—	0.04	0.19	0.04
TiO ₂	0.56	0.64	0.16	0.65	0.32	0.61
P ₂ O ₅	0.15	—	sp.	0.19	0.39	0.25
MnO	0.06	—	—	sp.	sp.	sp.
BaO	0.04	—	—	0.07	0.10	—
Som	99.58	100.02	99.47	99.84	99.77	100.36

- I Yentnite, Yentna River, Alaska; anal. H. N. STOKES, cf. J. E. SPURR, *Am. Journ. Sci.* X, 310, 1900 (Tonalose; included in the sum: S = 0.02, and traces of Cl, SrO, Li₂O).
- II Biotiteamphiboleandesite, right bank of Tëbaoeng-river, opposite N^a. Oeroei, Central-Borneo, anal. M. DITTRICH. (Tonalose).
- III Andesite, Punta della Civitate, Capraja-isl., Italy, anal. A. RÖHRIG, cf. H. EMMONS, *Quart. Journ. Geol. Soc.* XLIX. 142, 1893 (Cl = 0.07; Tonalose).
- IV Hypersteneaugiteandesite, Palisades, Crater Lake, Oregon, anal. H. N. STOKES, cf. H. B. PATTON, *Bull. U. S. Geol. Surv.* 168, 223, 1900 (SrO = 0.07; Tonalose).
- V Hornblendeporphyrite, Nevada City, Calif., anal. H. N. STOKES, cf. W. LINDGREN XVII *Ann. Rep. U. S. Geol. Surv.* II, 59; 1896 (SO₃ = 0.10, Tonalose).
- VI Pyroxenemicadiorite, Electric Peak, Yellowstone Nat. Park.; anal. W. H. MELVILLE, cf. J. P. IDDINGS, XII *Ann. Rep. U. S. Geol. Surv.* I, 627, 1891 (NiO = 0.09, Tonalose).

IV. *Aplitic Microgranite* (normat. Graniphyrilassenose).

The rough, pure white, powdery, very fine-grained rock often contains holes, in which appear mica-rosettes and serpentinous products, which also in microscopic aggregates lie scattered through the whole rock and by this betray a certain porosity.

The proper rock-components are mostly rather fresh and in keeping with this the appearance of the secondary products — among which the muscovite takes a foremost place — seems with great probability to have to be attributed to pneumatolytic processes, not to atmospheric weathering. The structure is holocrystalline porphyric, but as such it is only to be recognized microscopically. The very few phenocrysts (average diam. 0.3 mm.) consist of *albite*; they show a little developed idiomorphy, are seldom twinned after the albite-law, but often occur irregularly grown together into groups of 2—3 individuals. A beginning of decomposition shows itself in the appearance of opaque globulites, principally arranged parallel to the cleavage-directions. Quartz and orthoclase-phenocrysts are entirely wanting. The holocrystalline *groundmass* consists of lathshaped, seldom tabular, strongly undulous, and always after the albite-law twinned, irregularly diverging, now and then parallelly arranged acid *plagioclases*, cemented by grains of *quartz* with sometimes tolerably pronounced idiomorphy, then, however, always peripherically cut asunder fringelike by feldspar, mostly, however, without indication of crystallographic boun-

daries, and further by somewhat orthoclase. The feldspar shows only a very slight beginning of decomposition; on the other hand, especially scales of secondary colourless mica, beside them serpentinous products and a few irregular crystals of secondary amphibole, together with a here and there condensing globulitic troubling, probably caused by limonite, are often met with in the groundmass. Primary bisilicates, therefore, seem to be entirely wanting in the rock; the plagioclastic character of the feldspar marks the rock as a basic aplitic facies of microgranite, rich in Na_2O .

The chemical analysis yielded :

	%	Mol. Prop.	magn.	orth.	alb.	anorth	cor.	hyp.	quartz
SiO_2	72.44	1.207	—	132	138	88	—	7	542
Al_2O_3	16.51	0.162	—	22	73	44	23	—	—
Fe_2O_3	0.24	0.001	1	—	—	—	—	—	—
FeO	0.52	0.007	1	—	—	—	—	6	—
MgO	0.05	0.001	—	—	—	—	—	1	—
CaO	2.47	0.044	—	—	—	44	—	—	—
Na_2O	4.54	0.073	—	—	73	—	—	—	—
K_2O	2.13	0.022	—	22	—	—	—	—	—
TiO_2	sp.	—	—	—	—	—	—	—	—
$\text{H}_2\text{O}-105^\circ$	0.13	—	—	—	—	—	—	—	—
$\text{H}_2\text{O}+105^\circ$	1.13	—	—	—	—	—	—	—	—
	100.16								

From which follows the following norm :

quartz	32.52	Q = 32.52	} Sal = 97.58
orthoclase	12.23		
albite	38.25	F = 62.71	
anorthite	12.23		
corundum	2.35	C = 2.35	
hypersthene	0.89	P } Fem = 1.12	
magnetite	0.23		M }

If we suppose the rock to be fresh, it takes a place in class I (Persalane); Subclass I (Persalane); Order 4 (Brittanare), Rank 2 (Toscanase); Subrank 4 (Lassenose). The question, whether it can be placed in the chemical system must be considered however in con-

nection with the discussed decomposition of the rock. As follows from the microscopic description, the considerable remainder of Al_2O_3 after saturation of K_2O , Na_2O and CaO in the feldspar molecules must at least for the greater part be attributed to the appearance of muscovite. If we take for muscovite the formula $\text{KH}_2\text{Al}_3(\text{SiO}_4)_3$ ¹⁾, the Al_2O_3 -remainder disappears with the presence of 5.84% orthoclase by the side of 9.15% muscovite. This last value, however, is exaggeratedly high. If however, in accordance with a microscopic estimate, a quantity of about 3% muscovite is assumed, and the remainder of the Al_2O_3 is equally divided over K_2O , Na_2O and CaO , in the supposition that these oxydes in the same measure have been removed by solutions, the following composition of the rock is obtained :

quartz	28.32	$Q = 28.32$	}	Sal = 95.60
orthoclase	12.79	$F = 67.28$		
albite	40.87			
anorthite	13.62			
muscovite	3.00		}	Fem = 1.12
hypersthene	0.89			
magnetite	0.23			
water	1.11			
Sum	100.83			

Now, if we leave muscovite, as of apparently secondary origin, out of consideration, still then the rock takes the same place in the chemical system :

$$\frac{\text{Sal}}{\text{Fem}} = \frac{95.60}{1.12} > \frac{7}{1}, \text{ Persalane}$$

$$\frac{Q}{F} = \frac{28.32}{67.28} < \frac{3}{5} \text{ and } > \frac{1}{7}, \text{ Brittanare}$$

$$\frac{\text{K}_2\text{O} + \text{Na}_2\text{O}^2)}{\text{CaO}} = \frac{23 + 78}{49} = \frac{101}{49} > \frac{5}{3} \text{ and } < \frac{7}{1}, \text{ Toscanase}$$

$$\frac{\text{K}_2\text{O}}{\text{Na}_2\text{O}} = \frac{23}{78} < \frac{3}{5} \text{ and } > \frac{1}{7}, \text{ Lassenose.}$$

Against the name of lassenose can no doubt no serious objections be raised.

Instead of hypersthene the rock contains amphibole and serpentine, the first of which minerals being very rare, whilst the last mentioned is

¹⁾ ROSENBUCH, Mikrosk. Physiogr. 1, 2. p. 262. 1905.

²⁾ To each of the K_2O , Na_2O and CaO -molecules 5 has been added, of which 4 K_2O molecules, however, go to the muscovite, which is left out of consideration here.

principally confined to the holes, taking as appears from the low MgO-quantity, no important place in the analyzed rock-sample.

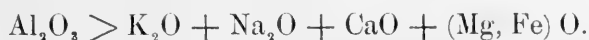
The molecular proportions yield, Fe_2O_3 being reduced to FeO and the whole being calculated on a sum of 100:

SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O
79.46	10.66	0.66	0.07	2.90	4.81	1.45

the formula according to OSANN:

	s	A	C	F	a	c	f	n	m	k	series
(OSANN)	79.46	6.26	3.63	—	12.66	7.34	—	7.7	—	1.73	α
(BECKE)	79.46	6.26	2.90	0.73	12.66	5.86	1.48			(10.0)	

Here we have the rare case that



If, like OSANN, we add MgO and FeO in the molecule $(\text{MgFe})\text{Al}_2\text{O}_4$ to C, there remains a rest of 0.77 Al_2O_3 ; if however like BECKE we neglect the Al_2O_3 remainder above $(\text{K, Na})_2\text{O} + \text{CaO}$, equal to 1.50, then $C = 2.90$ and $F = 0.73$. The calculation of $a + c + f = 30$ yields:

	a	c	f
(OSANN)	18.99	11.01	—
(BECKE)	18.99	8.79	2.22

In the graphic notation IV denotes the place of the rock; the filled circle the values after OSANN, the not-filled circle the one after BECKE.

Botany. — “*Some systematic and phytogeographical notes on the Javanese Casuarinaceae, especially of the State Herbaria at Leiden and at Utrecht.*” (Contribution to the knowledge of the Flora of Java. N^o. III).¹⁾ By Dr. S. H. KOORDERS.

§ 1. *Casuarina equisetifolia*, Forst.

§§ 1. Geographical distribution outside Java: according to Hook, Flora Br. Ind. V. 598: in British India on the East side of the Gulf of Bengal, South of Chittagong, in the Malay Archipelago, in Polynesia and in Australia. In the State Herbarium at Leiden I saw, however, also specimens from Madagascar, Mauritius, Bourbon and Senegambia, although it did not appear with certainty from the herbarium-labels, that they referred to uncultivated plants. In Herb. Leiden the species is also represented by specimens from

¹⁾ Continued from Transactions (Verhandelingen) Roy. Acad. Sciences Amsterdam Second Section Vol. XIV. (1908). N^o. 4.

Hawai and from Australia; in this case one of two specimens (from Sieber) which appear to me to be quite similar, has been determined by MIQUEL as *C. equisetifolia* FORST. and the other as *C. leptoclada* MIQ. In DIELS [Die Pflanzenwelt von West-Australiën südlich des Wendekreises (1906)] the occurrence of some other species of *Casuarina* is mentioned, but not of *C. equisetifolia*. Prof. Dr. I. DIELS was so kind as to supply me with the following information on this point: "Casuarina equisetifolia kommt in West-Australiën sicher nicht vor. Ob er in Ost-Australiën wächst habe ich persönlich nicht festgestellt, da ich mich dort nur kürzere Zeit aufhielt. Das von Ihnen erwähnte Exemplar, leg. Sieber, stammt aus der Gegend von SYDNEY, denn dort hat Sieber gesammelt." (Diels msc. 21. IV. 1908). From the Malay Archipelago outside Java I saw *C. equisetifolia* represented in the Herbaria at Leiden and at Utrecht from the following places: Sumatra (leg. KORTHALS; TEIJSMANN & DE VRIESE). Timor (FORBES n. 3746), Moluccas (REINW.), the North of Dutch New-Guinea (Expedition of WICHMANN, determ. VALETON). The examples from Sumatra, collected by KORTHALS, generally have 8 teeth, as MIQUEL already noted for these specimens. In N. E. Celebes the species is not found wild: there I only found *C. Rumphiana* MIQ.¹⁾

§§ 2. Geographical distribution and oecological conditions in Java: I have never found *C. equisetifolia* growing wild except in Western-Java in the S.W. of the residency Banten in the division Tjaringin near the village of Tjemara, and there only on a sandy sea-shore, on a small peninsula (= oedjoeng, malay) at sea-level, growing socially.

This may serve as a correction of the statement in KOORD. and VALETON "Boomsorten Java" X (1904) p. 273 (line 12 from top): "Tjemara (Banten) altit. 200 M. supra mare."

JUNGHUHN says in his Java. I. 2nd edit. (1853) 272: "Were we concerned in dealing with Sumatra, we should have to mention among the trees which grow in groups in the shore forests the Tjemara laoet: *Casuarina equisetifolia* Forst (*muricata* Roxb); nowhere, however, have I found this beach-Casuarina, although natives have assured me, that it is found in some places on the North coast of Krawang" (JUNGHUHN l. c.). It appears, however, that probably JUNGHUHN afterwards succeeded in finding this species wild in Java, namely on the Lawoe, although I have not been able to find anything

¹⁾ KOORDERS, S. H., Eerste Overzicht d. Flora N. O. Celebes (1898) 616; cf. KOORDERS and VALETON. Bijdrage Booms. Java X. (1904) 172 (Mededeelingen Lands Plantent. n^o. 19 en 68).

in any publication about this geographically interesting discovery. My surmise is founded on a specimen labelled by JUNGHUHN himself as follows: *Casuarina equisetifolia*, 'E monte Lawoe ubi sponte crescit'. This specimen must indeed be regarded as *C. equisetifolia* FORST. according to an autograph determination-label of MIQUEL. I found this specimen in the Leiden Herbarium, registered as H. L. B. n. 10 (899—173) and can confirm the accuracy of the determination of JUNGHUHN and of MIQUEL, for I found on the young branches of JUNGHUHN's specimen, which already bore fruit, that of 14 leafwhorls which I examined, 13 had 7 vaginal teeth and 1 only 6 teeth; the fruit had 12 longitudinal rows. There can therefore be no doubt that this specimen of JUNGHUHN from the Lawoe mountains is completely conspecific with the beach-Casuarina (*C. equisetifolia* FORST.), the more so, since also all other characteristics, e.g. the deeply grooved internodes, $\frac{1}{2}$ — $\frac{3}{4}$ cm. long and $\frac{1}{2}$ mm. thick, agree completely with this species. This is the first observed case, so interesting phytogeographically, of the beach Casuarina (*C. equisetifolia*) growing wild in the mountains of Java. The height of this station above sea level is not indicated by JUNGHUHN on the label quoted above. The other Javanese specimens of the State Herb at Leiden and at Utrecht, found by me, are: "Java, on the beach near Batavia and Anjol (leg. JUNGH.); Java (KORTH.; REINW.; TEIJSM.). In the Herbarium at Buitenzorg there are according to KOORD. and VALETON [Bijdr. Booms. Java X (1904) 271] some specimens from the Rahoen-Idjen mountains in Eastern Java, which mostly have 8 vaginal teeth. It appears to me, that we are quite as justified in placing these specimens from the Idjen-plateau under *C. equisetifolia*, as MIQUEL (see above) in the case of the generally 8-toothed beach-Casuarina of the West coast of Sumatra, and KOORDERS and VALETON (l. c. 271) in the case of the beach-Casuarina of S.W. Banten in Western Java, which generally has 7—8 teeth. If the specific limits between *C. montana* and *C. equisetifolia* be drawn as indicated, the distribution of *C. equisetifolia* in Java is as follows: Western Java: in the S.W. of the residency Banten, at sea-level, on a sandy sea-shore on a narrow peninsula (= oedjoeng), at the edge of the surf, growing socially (Herb. Kds in Mus. Bot. Hort. Bogor.). Central Java on the Lawoe growing wild, together with *C. montana* (Herb. JUNGHUHN in Leiden). Eastern Java: in the Rahoen-Idjen mountains, also growing wild with *C. montana* (Herb. Kds in Mus. Hort. Bogor.). Oecological conditions: Limited to soils, which always have little water or which are physiologically dry (containing much salt). Completely wanting on fertile soils, probably because it is

crowded out by other species. Although preferably growing wild on sandy sea-shores, and nearly always forming homogeneous woods, it is always wanting in the Javanese Mangrove forests. The tree resists direct sunlight very well, but deep shade very badly. On calcareous soils and in the Javanese Teak-forests it has not yet been observed wild. The species is also completely absent from the mixed, shady, evergreen forests of Java. Evidently it can only maintain itself in the struggle with other species in the above-named unfavourable localities.

§ 2. *Casuarina equisetifolia* Forst. var. *longiflora*, MIQ. ! Flora Regensburg. (1865) p. 17 ; MIQ. ! in DC. Prodr. XVI. 2 (1868) 339 ; BOERLAGE ! Handleid. Flora N. I. III. 1. (1900) 404 ; KOORD. and VALETON Bijdr. Booms. Java X. (1904) 272.

For this variety MIQUEL l. c. gave i. a. the diagnosis: "amentis masculis elongatis glabris; . . . vaginis 7-dentatis" and as locality "Java" (BLUME !) without further detail. From the authentic material found by me in the State Herbaria at Leiden and at Utrecht, the following results. The number of vaginal teeth is sometimes 7, as indicated by MIQUEL l. c. but is often also 6, and sometimes also 8. The male catkins are characterized by the complete absence of hairs, and by their sometimes attaining the exceptionally great length of 40—50 millimetres. On the authentic label the locality is only indicated in BLUME's handwriting as: "in Javae orient. montibus".

A specimen found by me without further indications in the Herbarium at Leiden, which had been sent in 1867 by TEYSMANN to HASSKARL, and, according to a note added by HASSKARL, was derived from a specimen standing in the Hortus Bogor. [in Herb. Lugd. Bat. sub n. 48 (899/173)], differs so little from the above named authentic specimen, that I suspect the authentic of *C. equisetifolia* FORST. var. *longiflora* MIQ. to be also derived from a cultivated specimen in the Buitenzorg Gardens. Both specimens greatly resemble *C. equisetifolia* FORST., but on account of the completely glabrous male catkins they are distinctly different from the type. The number of vaginal teeth in TEYSMANN's specimen is 7—8, and as in the authentic specimen 6—8.

I further found that not a single of the numerous other Javanese specimens of *Casuarina* in the herbaria at Leiden and at Utrecht, refer to this variety. I have never found the variety wild in Java.

To sum up, I consider it probable, that in this case of *Casuarina equisetifolia* var. *longiflora* MIQ. an error of BLUME's is the cause of the reputed indigenous occurrence of this plant in Java, an error similar in kind to that which was formerly demonstrated ¹⁾ in the case of another tree cultivated in Hortus of Buitenzorg; it appears, that this variety must be deleted from the flora of Java.

§ 3. *Casuarina montana*, JUNGH.! ex MIQ. Fl. Ind. Bat. I. 1. (1855) 875 (cum descript.); JUNGH.! Java I. ed. 2. (1853) 551—554, 631—639, 663; *C. montana*, LESCHEN. ex MIQ.! in ZOLL. Verzeichn. (1854) 86 (nomen tantum); *C. montana*, MIQ.! in A. DC. Prodr. XVI. 2. (1868) 335; MIQ. Illustr. Arch. Ind. (1871) 9. tab. 7. f. 1 et 2; KOORD. et VAL. Bijdr. Booms. Java X. (1904). 273!; *C. Junghuhniana*, MIQ! Plantae Junghuhnianae I. (1854) 7; MIQ.! Fl. Ind. Bat. I. 1. (1855) 874; JUNGH.! l.c. (1853) 551.

It is evident from the above bibliography, that according to the latest rules of nomenclature this species should not be named *C. montana* MIQ., as in KOORD. and VAL. l.c., nor *C. montana* LESCHEN., as in the Index Kewensis, but *C. montana* JUNGH.

§§ 1. Geographical distribution outside Java: Bangka (TEJSMANN n. 7650); Timor (ZIPP.; TEJSM.; FORBES n. 3512); Molucc. (REINW. n. 1504). — On the authentic specimen of ZIPPEL (in H. L. B.) I found on young branches of flowering shoots 10—11 vaginal teeth and generally 11 teeth; internodes 1—1 $\frac{1}{3}$ mm. thick and about 1 cm. long.

Two fruiting specimens from Timor, named by MIQUEL himself as *C. montana* have 11—12 teeth, like the var. *validior* MIQ., but with thin internodes, corresponding to the var. *tenuior* MIQ. — The fruiting specimen of REINWARDT from the Moluccas (without further indication of locality) had ten vaginal teeth throughout and corresponds, also as regards the diameter of the internodes, to the var. *tenuior*. — The fruiting specimen from Bangka bears in SCHEFFER's handwriting the manuscript name *C. equisetifolia* FORST. var. *bancana*; it has consistently 9 vaginal teeth, fruit cones with about 18 longitudinal rows, cylindrical internodes, $\frac{1}{2}$ — $\frac{3}{4}$ mm. thick about 1 cm. long, and not deeply grooved. This specimen from Bangka cannot in my opinion be separated from some specimens of the Javanese *C. montana*

¹⁾ Compare the distribution of *Quercus Pinanga* BL. in KOORD and VALETON. Bijdr. Booms. Java X (in Meded. Lands Plant. LXVIII 1904) p. 65 and in KOORD. Contribution No. 1 to the knowledge of the Flora of Java in Proc. Roy. Acad. Sciences. Amsterdam 28 March 1908 p. 772.

var. *tenuior* MIQ. — *C. montana* var. *validior* MIQ. I did not find represented in the Herbaria at Leiden and at Utrecht from regions outside Java.

§§ 2. Distribution in Java. The var. *validior* MIQ. I found represented in the Herb. at Leiden and Utrecht by the following specimens: 1) collected by JUNGHUHN according to his autograph note on the top of mount Kawi [the second label "Oengaran" which evidently was attached to the specimen at a later date, independently of JUNGHUHN, cannot, in my opinion, refer to this authentic specimen, for on mount Oengaran not a single *Casuarina* occurs wild]; 2) specimens from Java (without further indications (from TEYSM. & DE VRIESE and 3) a fruiting specimen from Java with the remark "Alpes orientales" (leg. WAITZ). In Herb. Kds the var. *validior* MIQ. is only represented by specimens from Mt. Wilis at 2000 m. altitude and from Mt. Ardjoeno at 2100—2400 metres; only the specimens from mount Ardjoeno are characteristic, for the determination of the variety of the specimens from the Wilis is not quite certain. The authentic specimen of JUNGHUHN from the top of Mt. Kawi (in Herb. Leiden) I found to have internodes of about 1 cm. long with a diameter of 1—1½ mm., and with 10—11 vaginal teeth. The specimen of WAITZ generally had 11 vaginal teeth. The Javanese examples of var. *tenuior* MIQ. are only represented in the Herbaria at Leiden and Utrecht by a few specimens of KORTHALS and of TEYSM. & DE VRIESE from "Java" (without further indications) and by a fruiting specimen (Kds. 37348 β Comm. ex museo bot. Hort. Bogor.), collected fruiting in October 1899 in Eastern Java on Mt. Tengger near Ngadisari at 2000 metres altitude. In the extensive alpine *Casuarina*-forests of Mt. Rahoen-Idjen in Eastern Java I found only var. *tenuior* MIQ. whereas var. *validior* appeared to be wholly wanting there. On Mt. Wilis in Central Java I found in the *Casuarina*-forests almost exclusively var. *tenuior* MIQ., but there nevertheless a small number of individuals belonging to var. *validior* MIQ. were also found; the form with internodes 1½ mm. thick, which is characteristic for the top of Mt. Kawi, could not be found on Mt. Wilis. The youngest twigs of var. *validior* MIQ., occurring on the latter mountain, where at most 1 mm. in diameter. JUNGHUHN mentions (Java. I (1853) p. 551), that *C. montana* first occurs on the Lawoe and thence eastwards covers the tops of all the mountains, which rise above 1500 metres, but is wholly absent from Western Java. As a result of my own observations I can confirm this statement. Concerning the

vertical distribution of *C. montana* var. *tenuior* MIQ. in the Wilis mountains on the Darawati summit in the residency Madioen, I append here, what I published on this subject in 1894 in a Dutch article "On the composition of some forests in the residency of Madioen" (in Tijdschr. v. Nijverh. en Landb. in N. Indië XLVIII (1894) part 4 p. 18—22 namely in the chapter "[To the top of the Wilis. Ascent of the Darawati]: "At 7⁴⁰ = 1670 m. altitude the mixed shady forest of high trees suddenly ceases, at least on the ridge, for in the valleys it continues further northwards and we arrive at a small alang-alang field with scattered young trees of *Albizzia montana* BENTH. and immediately after this we see the first specimens of *C. montana* JUNGH".

From this point, at about 1700 m. altitude, the ridge, which leads to the summit of the Darawati, is completely covered with this tree alone. On the slopes (and even almost right up to the ridge) other trees grow, up to an altitude of 2000 meters. Not until this altitude is reached, do *Casuarina*'s occur in the valleys." [KOORD. l. c. (1894) p. 19—20 of the reprint]. From this it results, that *Casuarina montana* var. *tenuior* is not found on mount Wilis below 1650 m. altitude, but that it occurs from there upwards to the highest top, at 2550 m. altitude. These data, and those about to be given, should be substituted for the figures of vertical distribution, published in KOORD. and VALETON Bijdr. Boomsoorten Java X (1904) p. 274.

I may further add, that also on journeys undertaken by me after the above-named year (1894) in the residency of Madioen, I *nowhere* found *C. montana* growing wild below 1650 m. altitude. It is indeed interesting, that this species at once forms forests, almost from the spot, where it first appears, and above 2000 m. not only covers the higher ridges, but also the valleys, almost to the exclusion of other trees. In the teakforests of Madioen, as in other parts of Java, I have only found *C. montana* and *C. equisetifolia* here and there cultivated (e. g. near pasanggrahans, along road-sides, etc.) but never growing wild. On the Idjen-plateau in the residency of Besoeki *C. montana* var. *tenuior* descends somewhat below the vertical limit of 1500 m. At this lower limit of distribution *C. montana* var. *tenuior* grows only on the dry mountain ridge, whereas it is crowded out from the ravines and moist places by other trees. On Mt. Tengger in 1899 I made the following note on the var. *tenuior*: A large tree attaining 35 m. with a trunk of 1½ m. in diameter; on steep rocks at 2000 m. altitude often only 20 m. high with a trunk 30 cm. diam. On Mt. Tengger forming forests, especially between 2200—

2800 m., but on the ridges of the N.E. side of the range descending to 1600 m. altitude.

Although adult trees cannot well stand deep shade, this does not apply to very young individuals. This is evident from the following note made by me in 1891¹⁾: Small trees of *Albizzia moluccana* BENTH., which had shot up after a forest fire in August 1891 on mount Wilis (in Java) at an altitude of about 1800 m., had were $1\frac{1}{2}$ —2 m. high, when I ascended the mountain on October 15th 1891, and there so crowded together, that these naturally grown Albizzia-woods resembled nursery beds. Under these, in fairly deep shade, I found numerous seedlings of *Casuarina montana*, growing wild and about 0.2 m. high.

The distribution and the oecological conditions of *C. montana* var. *tenuior* may be characterized as follows: Extraordinarily great power of resisting drought, strong winds and the strong direct sunlight of the alpine region, and, but only in earliest youth (*not* later) power of resisting shade. Very common in Central Java at 1650—3000 m. and in the eastern part of Eastern Java at about 1400—3000 m. altitude, but wild growing quite unknown west of mount Lawoe, indigenous not known either from the mount Oengaran [in contradiction to the inaccurate statement of MIQUEL in his Flora Ind. Bat. I. 1. p. 875].

§ 4. Means of distribution of *Casuarina equisetifolia* and *C. montana*.

Both species appear to be well adapted for distribution by wind, and in spite of the negative results of GUPPY's floating experiments, they seem also adapted for distribution by ocean currents.

In the winged fruit of Javarese specimens, examined by me, I observed the following dimensions. *C. equisetifolia* FORST.: fruits $1\frac{1}{2}$ —2 mm. long and $1 - 1\frac{1}{2}$ mm. broad compressed laterally, with a very thin, obovate wing, 5 mm. long and 3 mm. broad. In *C. montana* var. *tenuior* MIQ.: fruits $1\frac{1}{2} - 1\frac{3}{4} \times 1 - 1\frac{1}{2}$ mm., strongly compressed laterally, with very thin ovate wing, $2 - 2\frac{1}{4}$ mm. long and $1\frac{1}{2} - 1\frac{3}{4}$ mm. broad.

In his well-known experiments, on the floating of fruits and seeds GUPPY found, that the fruit cones of *Casuarina equisetifolia* FORST. remain floating on a $3\frac{1}{2}$ percent solution of common salt for 1—2 days at the most. This period is not, however, sufficient to account for the known, wide over-sea distribution of this species. On repeating the experiment of GUPPY, I could only confirm the shortness of the

¹⁾ Compare KOORD. and VALETON Bijdr. Booms. Java II. (1895) 294.

floating period for separate fruit cones. I found, however, that the floating period on a similar salt solution is so much greater for fruitlets, which have been liberated from the cone (e. g. by dessication), that the wide distribution now becomes quite intelligible, if one but supposes, that the germinative power is not damaged by a sojourn of one month in sea-water. On this point, however, no experiments have as yet, to my knowledge been made. Meanwhile I feel justified in deducing from the anatomical structure of the fruitlets, that the embryo is most probably sufficiently protected against the entry of sea-water. In some flotation experiments I found that after one month 100% of the fruitlets of *C. equisetifolia* FORST., and upwards of 75% of those of *C. montana* JUNGH. var. *tenuior* MIQ. remained floating.

Besides by anemophilous and hydrophilous distribution, *C. equisetifolia* and *C. montana* can spread by rootsuckers. The latter are however rarely found in these species further than 10 m. from the main trunk. Should the main trunk die off (for instance in consequence of a fire) one can often observe, e. g. with *C. montana*, that a young copse round the dead trunk has grown up from these root-suckers. The distribution over very large intervals of sea, however, no doubt takes place in *Casuarina montana* and *C. equisetifolia* by means of the winged fruits, first through wind transport and then through ocean currents.

§ 5. On a monstrosity of *Casuarina*.

In the Herbarium at Leiden I found a specimen, which had been labelled by BOERLAGE as a monstrosity, collected by JUNGHUHN in Java [in H. L. B. sub. n. 50 (899—173)]. This malformation proved to be a fruiting branch, resembling a witches' broom (in German "Hexenbesen") and belonging to *Casuarina montana* var. *tenuior* MIQ. Besides the above mentioned aberrant mode of branching, this specimen shows the peculiarity, that the axis of all its fruit cones has continued to grow. The axis, thus continued, gives the characteristic appearance to the shoots; are these branched like a witches' broom, have abnormally thickened internodes and bear abnormally developed leafsheaths. The shoots in question also bore a small number of normally formed young twigs and thus the determination was possible to me. These normal branches, have regular cylindrical internodes, about 1 cm. long and $\frac{3}{4}$ —1 mm. thick, generally with 11 vaginal teeth, as is often the case in the above variety. I was unable to find a fungus or other cause for the formation of these witches' brooms in the herbarium-specimen referred to.

§ 6. Phylogenetic note on *Casuarina montana* Jungh. and on
C. equisetifolia Forst.

In the Herbaria at Leiden and at Utrecht I found herbarium-specimens of young seedlings and of very young shoots, developed from adventitious buds.

Accompanying one of the former specimens I found a manuscript note by MIQUEL, to the effect that these young seedlings had been raised from seed of *Casuarina montana*, imported in 1846 from Java to the Hortus at Rotterdam. These seedlings have on their youngest twigs internodes of about 2 mm. length and $\frac{1}{3}$ mm. diameter, with 4—5 deep grooves; in the 24 leaf sheaths examined by me, the number of vaginal teeth was as often 4 as 5, but never more and never less. The accompanying note of MIQUEL, indicates, however, that although 4—5 vaginal teeth were most common, he had also observed 6 teeth. The teeth are narrowly lanceolate and finely acuminate. The stems of these seedlings are only $2\frac{1}{2}$ —3 mm. in diameter. MIQUEL has added in autograph: "*Casuarina montana* (*non alior*)" and below also *C. Brunoniana*. The species *C. Brunoniana*, which MIQUEL had described from young hot-house plants from the Rotterdam and Berlin Gardens, afterwards proved to be nothing but the "Jugendform" of *Casuarina equisetifolia* and *C. montana*. From two authentic specimens of this species in the Herbarium at Utrecht, I could see that MIQUEL himself has withdrawn his *C. Brunoniana*, and regarded it partly as *C. equisetifolia* and partly as *C. montana*. It appears to me possible, however, that all the specimens named by MIQUEL *C. Brunoniana* belong to *C. montana* JUNGH. only. For the young specimens, named by MIQUEL as *C. equisetifolia* agree well with this. Of young seedlings, which are derived with certainty from *C. equisetifolia*, I have here no material at my disposal for investigation. In Java I have only observed the constant unusually small number of vaginal teeth in young seedlings of *C. montana*, of the var. *tenuior*. In the very young seedlings I examined, the number was never more than 4—6 as in the seedlings of *C. Brunoniana* of the Utrecht Herbarium.

Concerning a herbarium specimen (Kds 37348 β in Herb. Lugd. Bat.) of *Casuarina montana* var. *tenuior* MIQ., collected in Oct. 1899 at 2000 m. altitude near Ngadisari on Mt. Tengger in Eastern Java, I observed the following: The specimen consists of ordinary fertile old branches, and of some young sterile shoots, which had evidently developed from adventitious buds, after an older thicker trunk had been cut down near the ground. These young

shoots were characterized by internodes of $\frac{1}{2}$ mm. diameter with 5—6 deep longitudinal grooves and only 5—6 vaginal teeth. On the other hand the youngest twigs, which had been formed on the ordinary ascending older branches of the same individual, had cylindrical internodes, not deeply-grooved, $\frac{3}{4}$ —1 mm. diameter, with 9—10 vaginal teeth. For the sake of completeness the morphologically unimportant, but physiognomically striking circumstance should be mentioned, that a great number of the youngest twigs of these young root-suckers were malformed at their tops to ovate or irregularly formed galls, about 3—5 mm. long and $2\frac{1}{2}$ —3 mm. thick. In these galls I could generally still detect the insect which had produced these malformations. It need scarcely be mentioned, that the above description of the morphologically aberrant structure of the twigs, refers only to normally constituted ones, and not to the pathological malformations on the rootsuckers, formed from adventitious buds. I may further allude to a specimen collected by TEYSMANN and DE VRIESE in 1859—1860 in Java? (without further indications as to locality) and labelled by MIQUEL "*Casuarina equisetifolia* FORST., *monstrosa*?" This specimen, found by me in the Herbarium at Leiden, appears to me to be quite similar to the one, described above, of the ordinary *Casuarina montana* var. *tenuior* MIQ., with young root-suckers, partly deformed by galls at the shoot-tops, the number of vaginal teeth in this specimen, examined by MIQUEL is (also in the youngest twigs not attacked by galls) invariably only 6—7, never more.

Summing up (and wholly leaving out of account the above-described malformations due to galls) we find briefly the following:

1. In these very young seedlings of *Casuarina montana* var. *tenuior* MIQ., some internodes are provided with 4, others with 5—6 deep longitudinal grooves, while the number of vaginal teeth is 4—6, (never more) and in the youngest stages only 4.

2. Very young shoots formed in *Casuarina montana* var. *tenuior* from adventitious buds in the base of the trunk, had similar deeper grooved internodes with 5—6 (never with more) vaginal teeth, like the young seedling mentioned sub 1.

3. It appears that in the species here in question (*C. montana*) the youngest developmental stages of the seedlings show phylogenetically older phases of development than the young shoots from adventitious buds of the trunk examined above.

4. The structure of the seedlings referred to sub 1 seems to point to both *Casuarina equisetifolia* FORST. and *C. montana* JUNGH. being mutants of parent forms with quadrangular internodes and 4 deep longitudinal grooves, with 4 vaginal teeth. Such forms, which in my

opinion are older (e. g. *C. nodiflora* FORST. and *C. sumatrana* JUNGH.) still survive for instance, in Australia, in Sumatra, Borneo, Celebes, and in the Moluccas, but recent forms are now wanting in Java, and fossil ones have not yet been found in Java.

5. Of the two Javanese indigenous species of *Casuarina*, *C. montana* JUNGH. appear to be phylogenitically younger than *C. equisetifolia* FORST.; the former species is probably a mutant, which has only maintained itself within the region of the Malay Archipelago, and which has arisen from the latter species.

6. Probably *C. montana* var. *validior* MIQ. is a mutant, which has maintained itself in Java only and which has arisen from *C. montana* var. *tenuior* MIQ.

Physics. — “Contribution to the theory of binary mixtures,” XI.

(Continued). By Prof. J. D. VAN DER WAALS.

Now we shall proceed to the investigation of some properties of the loci of the points of intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$, in the first place when this locus is a closed figure, lying wholly at volumes larger than b . Let us write.

$$(v - b)^2 + x(1-x) \left(\frac{db}{dx}\right)^2 = x(1-x) \frac{c}{a} v^2$$

in the form:

$$v^2 \left\{ 1-x(1-x) \frac{c}{a} \right\} - 2vb + \left\{ b_1^2 + x(b_2^2 - b_1^2) \right\} = 0. \quad (\varphi)$$

The form of the third term in this equation appears only to depend on the first power of x , because $b^2 + x(1-x) \left(\frac{db}{dx}\right)^2$ may be written $b_1^2 + 2xb_1 \frac{db}{dx} + x^2 \left(\frac{db}{dx}\right)^2$ and to this added $x(1-x) \left(\frac{db}{dx}\right)^2$. The third term then becomes $b_1^2 + \frac{db}{dx} \left(2b_1 + \frac{db}{dx} \right) x$, in which $\frac{db}{dx} = b_2 - b_1$.

If we put $x(1-x) \frac{c}{a} = A$, the equation (φ) becomes

$$v^2(1-A) - 2vb + b_1^2 + x(b_2^2 - b_1^2) = 0 \quad . \quad . \quad (\varphi')$$

Let us seek the points of this line in which the tangent is parallel to the x -axis, and so in which $\frac{dv}{dx} = 0$; then we find another equation

by differentiating φ' with respect to x , and by keeping v constant, viz.:

$$-v^2 \frac{dA}{dx} - 2v(b_2 - b_1) + b_2^2 - b_1^2 = 0 \dots \dots (\varphi'')$$

By eliminating v from (φ') and (φ'') , we obtain an equation in x only — and for the values of x which satisfy this resulting equation, $\frac{dv}{dx}$ will be $= 0$. We shall, however, seek a resulting equation in x in a somewhat different way.

If we subtract $x(\varphi'')$ from (φ') , we get:

$$v^2 \left\{ 1 - A + x \frac{dA}{dx} \right\} - 2vb_1 + b_1^2 = 0,$$

and adding this last equation to (φ'') , we get:

$$v^2 \left\{ 1 - A - (1 - x) \frac{dA}{dx} \right\} - 2vb_2 + b_2^2 = 0.$$

Hence:

$$\frac{b_1}{v} = 1 \pm \sqrt{A - x \frac{dA}{dx}}$$

and

$$\frac{b_2}{v} = 1 \pm \sqrt{A + (1 - x) \frac{dA}{dx}}.$$

Now $\frac{b_1}{v}$ is certainly smaller than 1, hence in the expression for $\frac{b_1}{v}$ only the sign — can be retained before the radical sign. And leaving undecided for the present whether $v > b_2$ or $v < b_2$, we find when we divide $\frac{b_2}{v}$ by $\frac{b_1}{v}$:

$$n = \frac{1 \pm \sqrt{A + (1-x) \frac{dA}{dx}}}{1 - \sqrt{A - x \frac{dA}{dx}}}$$

or

$$n - 1 - n \sqrt{A - x \frac{dA}{dx}} \mp \sqrt{A + (1-x) \frac{dA}{dx}} = 0. \quad (\varphi''')$$

Now

$$A + (1-x) \frac{dA}{dx} = (1-x)^2 \frac{c}{a} \left\{ 1 - \frac{x}{a} \frac{da}{dx} \right\}$$

and

$$A - x \frac{dA}{dx} = x^2 \frac{c}{a} \left(1 + \frac{1-x}{a} \frac{da}{dx} \right)$$

The first member of equation (φ''') becomes for $x=0$:

$$n - 1 \mp \sqrt{\frac{c}{a_1}}$$

or

$$n - 1 \mp \frac{n - 1}{\sqrt{1 + \varepsilon_1}}$$

and so, whether the sign $-$ or the sign $+$ is chosen, always positive, if as in the case considered, the quantity ε_1 is positive. For $x=1$ the first member of (φ''') becomes equal to:

$$(n - 1) - n \sqrt{\frac{c}{a_2}}$$

or

$$n - 1 - \frac{n - 1}{\sqrt{1 + \varepsilon_2}}$$

This value would be negative when, as will be supposed in a following case, ε_2 is negative — but it is also positive, if as is now the case, ε_2 is positive. If the sign of the value of the first member of (φ''') is different for $x=0$ and $x=1$, then there will be a value of x between 0 and 1 satisfying (φ'''). But in our case the first member of (φ''') has the same sign for $x=0$ and $x=1$. From this it does not follow, of course, that there exists no root for (φ'''), but only that this equation either has no roots or an even number. This equation has no roots when the locus is imaginary — but if the latter exists, as is the case when $1 > \frac{\sqrt{\varepsilon_1 + n\sqrt{\varepsilon_2}}}{n-1}$, and when the

locus is a closed figure, then there must be two. If the value of the first member of (φ''') is graphically represented between $x=0$ and $x=1$, the curve representing this value, begins and ends positive. If this value passes to negative values, it must have an ordinate equal to 0 at least twice, and so also assume a minimum value. Hence if there are two values of x satisfying (φ'''), the equation obtained by differentiating (φ''') with respect to x , must have a root.

Now $\frac{d(\varphi''')}{dx}$ is equal to:

$$- \frac{n}{2} \frac{-x \frac{d^2 A}{dx^2}}{\sqrt{\left\{ A - x \frac{dA}{dx} \right\}}} \mp \frac{1}{2} \frac{(1-x) \frac{d^2 A}{dx^2}}{\sqrt{\left\{ A + (1-x) \frac{dA}{dx} \right\}}}$$

So for the minimum value of (φ''') this equation must be equal to 0.

This expression is equal to 0, if $\frac{d^2 A}{dx^2} = 0$, or if:

$$\frac{nx}{\sqrt{\left(A - x \frac{dA}{dx}\right)}} = \pm \frac{1-x}{\sqrt{\left\{A + (1-x) \frac{dA}{dx}\right\}}}$$

The latter can only be the case, if in the second member the sign $+$ is retained, and $-$ is rejected. This means that in the expression:

$$n = \frac{1 \pm \sqrt{\left\{A + (1-x) \frac{dA}{dx}\right\}}}{1 - \sqrt{\left\{A - x \frac{dA}{dx}\right\}}}$$

only the sign $+$ must hold in the numerator of the second member, or that $\frac{b_2}{r} > 1$. So if the closed curve is restricted to volumes smaller than b_2 .

If we seek the value of x which satisfies:

$$\frac{n^2 x^2}{A - x \frac{dA}{dx}} = \frac{(1-x)}{A + (1-x) \frac{dA}{dx}}$$

then when this value of x is substituted, (φ''') must be negative, because (φ''') has proved to be positive for $x = 0$ and $x = 1$.

For it is not sufficient for the existence of 2 roots of the equation $\varphi''' = 1$ that φ''' has a minimum value, but it is also required that this minimum value is negative.

If we substitute in:

$$n - 1 - n \sqrt{\left\{A - x \frac{dA}{dx}\right\}} - \sqrt{\left\{A + (1-x) \frac{dA}{dx}\right\}}$$

the value of:

$$\sqrt{\left\{A - x \frac{dA}{dx}\right\}} = \frac{nx}{1-x} \sqrt{\left\{A + (1-x) \frac{dA}{dx}\right\}},$$

then:

$$n - 1 - \frac{n^2 x + (1-x)}{1-x} \sqrt{\left\{A + (1-x) \frac{dA}{dx}\right\}}$$

must be negative.

Now we find from the condition on which φ''' has a minimum value:

$$\frac{dA}{dx} = A \frac{(1-x)^2 - n^2 x^2}{x(1-x)\{1-x+n^2 x\}}$$

and

$$A + (1-x) \frac{dA}{dx} = A \frac{(1-x)^2}{(1-x+n^2x)x(1-x)} = \frac{c}{a} \frac{(1-x)^2}{1-x+n^2x}$$

Hence

$$(n-1) - \sqrt{\frac{c}{a} \{1-x+n^2x\}}$$

must be negative.

Now if we write $a = a_1(1-x) + a_2x - cx(1-x)$ and $\frac{a_1}{c} = \frac{1+\varepsilon_1}{(n-1)^2}$

and $\frac{a_2}{c} = n^2 \frac{1+\varepsilon_2}{(n-1)^2}$, then

$$(n-1) - (n-1) \sqrt{\frac{1-x+x^2x}{(1-x)(1+\varepsilon_1) + xn^2(1+\varepsilon_2) - (n-1)^2x(1-x)}}$$

must be negative. This will be the case if under the radical sign the numerator is larger than the denominator, or if:

$$(1-x)(1+\varepsilon_1) + n^2x(1+\varepsilon_2) - (n-1)^2x(1-x) < 1-x+n^2x$$

or

$$(1-x)\varepsilon_1 + n^2x\varepsilon_2 - (n-1)^2x(1-x) < 0$$

or

$$\frac{\varepsilon_1}{(n-1)^2} - x \left\{ 1 + \frac{\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2} \right\} + x^2 < 0.$$

The extreme values of x of the closed curve are given by the equation:

$$\frac{\varepsilon_1}{(n-1)^2} - x \left\{ 1 + \frac{\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2} \right\} + x^2 = 0.$$

If the first member of this equation is negative, the values of x satisfying the same value, are nearer together, as was to be expected.

We have reduced the condition that φ''' be negative in its minimum value to:

$$\frac{\varepsilon_1}{(n-1)^2} - x \left\{ 1 + \frac{\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2} \right\} + x^2 = -\Delta,$$

if Δ is a positive quantity. If this is to be the case for real values of x , then (ε_1 and ε_2 positive),

$$\left\{ 1 + \frac{\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2} \right\}^2 > \frac{\varepsilon_1}{(n-1)^2}$$

must be, or

$$1 - \frac{\sqrt{\varepsilon_1} + x\sqrt{\varepsilon_2}}{n-1} > 0.$$

This condition is fulfilled when the points of which ε_1 and ε_2 are

the coordinates, lie in the region for which the locus considered is a closed curve.

So we may sum up what has been demonstrated as follows. We have derived $\frac{(d\psi''')}{dx} = 0$ from $(\psi''') = 0$, and stated the condition on

which ψ''' becomes negative by the substitution of $\frac{d\psi'''}{dx} = 0$. Strictly

speaking we should still have to show that $\frac{d\psi'''}{dx} = 0$ has real roots

— and moreover that the value of these roots is in accordance with the result obtained. Let us, for this purpose, examine what follows concerning the value of x which satisfies the equation obtained

before, which we derived from $\frac{d\psi'''}{dx} = 0$, viz.:

$$\frac{dA}{dx} = A \frac{(1-x)^2 - n^2 x^2}{x(1-x)[1-x+n^2 x]}$$

Now $\frac{dA}{dx} = \frac{c[a_1(1-x)^2 - a_2 x^2]}{a^2}$ and $A = \frac{cx(1-x)}{a^2}$ and after reduction we find:

$$\frac{-a_1 n^2 + a_2}{c} = (1-x)^2 - n^2 x^2$$

or

$$\frac{n^2(\varepsilon_2 - \varepsilon_1)}{(n-1)^2} = (1-x)^2 - n^2 x^2$$

For x between 0 and 1 the second member of this equation has a value of n which descends continually and lies between 0 and $-n^2$. So there will be a root if $\frac{n^2(\varepsilon_2 - \varepsilon_1)}{(n-1)^2} < 1$ and $> -n^2$. Or if

$$\varepsilon_1 > \varepsilon_2 - \left(\frac{n-1}{n}\right)^2$$

and

$$\varepsilon_1 < \varepsilon_2 + (n-1)^2$$

If we trace two lines at an angle of 45° with the axes through the points P and Q , then $\varepsilon_1 < \varepsilon_2 + (n-1)^2$ and $\varepsilon_1 > \varepsilon_2 - \frac{(n-1)^2}{x^2}$

implies that $\frac{dA}{dx}$ has one real root between $x = 0$ and $x = 1$ for all points between these two lines. If we confine ourselves to positive values of ε_1 and ε_2 , this space comprises a very large part of the first parabola, and moreover the space which I shall indicate by OPQ

between the parabola and the axes. If we put $(1-x)^2 = \frac{n^2 \varepsilon_2 + k}{(n-1)^2}$ and $n^2 x^2 = \frac{n^2 \varepsilon_1 + k}{(n-1)^2}$, these two equations, when k has been properly determined, will hold for the value of x of the root. By application of $(1-x) + x = 1$, we bring the condition for the determination of k in the following form:

$$\frac{n \sqrt{\varepsilon_2 + \frac{k}{n^2}}}{n-1} + \frac{\sqrt{\varepsilon_1 + \frac{k}{n^2}}}{n-1} = 1.$$

If for the binary mixture ε_1 and ε_2 were such that:

$$\frac{n\sqrt{\varepsilon_2}}{n-1} + \frac{\sqrt{\varepsilon_1}}{n-1} = 1$$

the point $(\varepsilon_1, \varepsilon_2)$ lies on the parabola, and the whole locus reduces to a point. But then it appears that for the root of $\frac{d(\rho''')}{dx} = 0$ the quantity k must be $= 0$, and that the value of x for this root coincides with the point in which the locus has contracted. If ε_1 and ε_2 have such a value that $\frac{n\sqrt{\varepsilon_2}}{n-1} + \frac{\sqrt{\varepsilon_1}}{n-1} < 1$, the point $\varepsilon_1, \varepsilon_2$ lies in the space OPQ , and there is a locus between two values x_1 and x_2 . If we add $\frac{k}{n^2}$ both to ε_1 and to ε_2 , then $\frac{k}{n^2}$ may be chosen in such a way that the condition $\frac{d(\rho''')}{dx} = 0$ is satisfied, and so also:

$$\frac{n \sqrt{\varepsilon_2 + \frac{k}{n^2}}}{n-1} + \frac{\sqrt{\varepsilon_1 + \frac{k}{n^2}}}{n-1} = 1$$

The addition of an equal amount to ε_1 and to ε_2 involves, of course, a shifting of the point $(\varepsilon_1, \varepsilon_2)$ in a direction which makes an angle of 45° with the axes, and that in such a way that the projection of the shifting on each of the axes is equal to $\frac{k}{n^2}$. We suppose k to be positive. So we find the value of k by taking n^2 times the amount which is to be added to the projections of the said point to reach the parabola. If the point $(\varepsilon_1, \varepsilon_2)$ lies in OPQ , k is positive. But for points within the parabola, k is negative. But as for the case that the closed locus exists, the point $(\varepsilon_1, \varepsilon_2)$ must lie inside OPQ , we have only to deal with positive values of k .

So we have $x > \frac{\sqrt{\varepsilon_1}}{n-1}$ and $1-x > \frac{n\sqrt{\varepsilon_2}}{n-1}$, and the equation :

$$\frac{\varepsilon_1}{(n-1)^2} + \frac{n^2\varepsilon_2}{(n-1)^2} = 1$$

holding for the values of x of the points of the locus, we find, after substitution of $x > \frac{\sqrt{\varepsilon_1}}{n-1}$ and $1-x > \frac{n\sqrt{\varepsilon_2}}{n-1}$:

$$\frac{\sqrt{\varepsilon_1}}{n-1} + \frac{n\sqrt{\varepsilon_2}}{n-1} < 1$$

a relation which exists indeed for points of the space OPQ below the parabola.

But now we have to make the following remark about the equation which indicates the value of x for the points where $\frac{dv}{dx} = 0$ for the closed curve. For this equation (φ''') we found the following form :

$$n-1-n\sqrt{\left\{A-x\frac{dA}{dx}\right\}} \mp \sqrt{\left\{A+(1-x)\frac{dA}{dx}\right\}} = 0$$

or

$$(n-1) - nx \sqrt{\frac{c}{a} \left\{1 + \frac{1-x}{a} \frac{da}{dx}\right\}} \mp (1-x) \sqrt{\frac{c}{a} \left\{1 - \frac{x}{a} \frac{da}{dx}\right\}} = 0.$$

If we seek the values of $\frac{a+(1-x)\frac{da}{dx}}{a}$ and of $\frac{a-x\frac{da}{dx}}{a}$, we find $\frac{a_2-c(1-x)^2}{a}$ and $\frac{a_1-cx^2}{a}$ for this. These quantities must be positive, because they occur under the radical sign. And this gives a restriction for the values of x for which $\frac{dv}{dx}$ can be $= 0$. If $a_2 > c$ the former of the values mentioned is positive for all the values from $x=0$ to $x=1$. The quantity $\frac{a_2}{c}$ is equal to $\frac{n^2(1+\varepsilon_2)}{(n-1)^2}$, and so certainly greater than 1 for positive ε_2 . The quantity $a_1 - cx^2$ is positive, when $x^2 < \frac{a_1}{c}$ and negative for $x^2 > \frac{a_1}{c}$. So if $\frac{a_1}{c} < 1$, values of x lying near 1, cannot exist. This will be the case, as soon as $1 > \frac{a_1}{c}$ or $1 > \frac{1+\varepsilon_1}{(n-1)^2}$, or $n^2 - 2n > \varepsilon_1$. If we put the

greatest value of x at which $\frac{dv}{dx} = 0$ can still occur $= x_g$, then $1 + \varepsilon_1 = x_g^2 (n - 1)^2$ $\varepsilon_1 = x_g^2 (n - 1)^2 - 1$, which value must be positive for ε_1 .

Now we may proceed to demonstrate that the minimum of (φ''') cannot be given by the second factor of $\frac{d(\varphi''')}{dx} = 0$, viz. by $\frac{d^2 A}{dx^2} = 0$;

and at the same time furnish a proof for the theorem that $\frac{dv}{dx} = 0$

can only occur for volumes smaller than b_2 . The quantity

$A = \frac{x(1-x)c}{a}$ begins with a value $= 0$ at $x = 0$, and ends also with

0 at $x = 1$. So there is a maximum value and we find it from

$\frac{dA}{dx} = \frac{c[a_1(1-x)^2 - a_2x^2]}{a^2}$ at $\frac{x}{1-x} = \sqrt{\frac{a_1}{a_2}}$. For this maximum

value of A $\frac{d^2 A}{dx^2} < 0$, and we should be apt to suppose that this

will be the case throughout the course from $x = 0$ to $x = 1$. This,

however, is not always the case. In some cases a point of inflection

appears in the line representing A at certain value of x , and then $\frac{d^2 A}{dx^2}$

is positive for greater value of x . If we calculate $\frac{d^2 A}{dx^2}$, we may

reduce it to the following form :

$$\frac{d^2 A}{dx^2} = -\frac{2c}{a^3} \left\{ a_1 a_2 - c [a_1 (1-x)^3 + a_2 x^3] \right\}$$

And now it is the question whether $a_1 a_2 - [a_1 (1-x)^3 + a_2 x^3]$

can be equal to 0 . For $x = 0$ this quantity is $a_1 [a_2 - c]$, and as

$\frac{a_2}{c} = \frac{n^2 (1 + \varepsilon_2)}{(n-1)^2}$, the value of $a_2 - c$ will certainly be positive for

positive ε_2 . Hence $\frac{d^2 A}{dx^2}$ is negative for $x = 0$. For $x = 1$ this quan-

tity is $a_2 (a_1 - c)$ and as $\frac{a_1}{c} = \frac{1 + \varepsilon_1}{(n-1)^2}$ and $\frac{a_1}{c} - 1 = \frac{1 + \varepsilon_1}{(n-1)^2} - 1$, we

can get a negative value for it if the value of ε_1 is small and that

of n large. This case occurs when $\varepsilon_1 < n^2 - 2n$. Then there is a

value of x for which $\frac{d^2 A}{dx^2}$ changes the negative sign into the positive

one. Now we saw, however, above, that if $\varepsilon_1 < n^2 - 2n$, the value

of $(\varphi''') = 0$ is not real over the full extent from $x = 0$ to $x = 1$. And now the question rises which value of x is greater: the value

at which φ''' becomes imaginary or the value of x at which $\frac{d^2A}{dx^2}$ becomes $= 0$. We can decide this at once by substituting $x_g = \sqrt{\frac{a_1}{c}}$, the limiting value for (φ''') real, in $\frac{d^2A}{dx^2}$. We find then:

$$\begin{aligned} \frac{d^2A}{dx^2} &= -2 \frac{c^3}{a^3} \left\{ \frac{a_1 a_3}{c} - \left[\frac{a_1}{c} (1-x)^3 + \frac{a_2}{c} x^2 \right] \right\} = \\ &= -2 \frac{c^3}{a^3} \left\{ x_g^2 \frac{a_2}{c} - x_g^2 (1-x_g)^2 - x_g \frac{a_1}{c} \right\} \end{aligned}$$

or

$$\frac{d^2A}{dx^2} = -\frac{2c^3}{a^3} x_g^2 (1-x_g) \left\{ \frac{a_2}{c} - (1-x_g) \right\}$$

As $\frac{a^2}{c} > 1$, and a fortiori $> (1-x_g)$, we find $\frac{d^2A}{dx^2}$ still negative.

Finally by availing ourselves of the values obtained we shall be able to verify that even if the function (φ''') is not real over the full extent from $x=0$ to $x=1$, and so if our conclusion that this function must possess a minimum value which is negative, can no longer be considered as proved, there is even in this case also a root for $\frac{d(\varphi''')}{dx} = 0$ at a value of x which is smaller than x_g , and which has therefore the former meaning for (φ''') .

For the root of $\frac{d(\varphi''')}{dx} = 0$ holds the equation:

$$\frac{a_2 - n^2 a_1}{c} = (1-x)^2 - n^2 x^2 \quad (\text{see page 431})$$

and so if $\frac{a_1}{c} = x_g^2$ is put, the following equation holds:

$$\frac{a_2}{c} - (1-x_g)^2 = (1-x)^2 - (1-x_g)^2 + n^2 (x_g^2 - x^2)$$

or

$$\frac{a_2}{c} - (1-x_g)^2 = (x_g - x) \{ 2 + (n^2 - 1)(x_g + x) \}$$

and as $\frac{a_2}{c} - (1-x_g)^2$ is positive, $(x_g - x)$ must also be positive, or the root of $\frac{d(\varphi''')}{dx} = 0$ lies at smaller value of x than that of the final

point of (φ''') . At the final point $(\varphi''') = 0$. At $x = 0$, (φ''') is positive. So for the intermediate minimum value (φ''') is negative.

The function $\varphi''' = 0$, the relation through which we may know the value of x for the points in which $\frac{dv}{dx} = 0$ for the closed curve, must also be satisfied by the value of x of the point in which the closed curve has contracted to a single point. To show this we have to substitute the values $x = \frac{\sqrt{\varepsilon_1}}{n-1}$ and $(1-x) = \frac{\sqrt{\varepsilon_2}}{n-1}$ in:

$$(n-1) - nx \frac{c}{a} (1-x) \sqrt{\frac{a_2}{c(1-x)^2} - 1} - (1-x) \frac{xc}{a} \sqrt{\frac{a_2}{cx^2} - 1} = 0$$

where it appears that this equation is satisfied. That we only retain the sign — for the third term is in accordance with our conclusion that $v < b_2$ for the whole curve. And that $\frac{dv}{dx} = 0$ must also be satisfied in the isolated point, — the point to which the whole curve has contracted, — follows from the circumstance that for such a point $\frac{dv}{dx}$ has an arbitrary value. The quantity $\frac{a}{cx(1-x)} = \frac{1}{A}$ is equal to:

$$\frac{a_1(1-2(+a_2x-cx, 1-2))}{cx(1-x)} = \frac{a_1}{cx} + \frac{a_2}{c(1-x)} - 1 = \frac{1+\varepsilon_1}{(n-1)\sqrt{\varepsilon_1}} + \frac{n(1+\varepsilon_2)}{(n-1)\sqrt{\varepsilon_2}} - 1$$

or

$$\frac{a}{cx(1-x)} = \frac{1}{\sqrt{\varepsilon_1}} + \frac{n}{\sqrt{\varepsilon_2}}$$

$$\text{Further } \sqrt{\frac{a_2}{c(1-x)^2} - 1} = \sqrt{\frac{1}{\varepsilon_2}} \text{ and } \sqrt{\frac{a_1}{cx^2} - 1} = \sqrt{\frac{1}{\varepsilon_1}}$$

Substituting these values we find:

$$(n-1) - \frac{(n-1)}{\frac{1}{\sqrt{\varepsilon_1}} + \frac{n}{\sqrt{\varepsilon_2}}} \left[\frac{n}{\sqrt{\varepsilon_2}} + \frac{1}{\sqrt{\varepsilon_1}} \right] = 0$$

Let us write the equation of the closed curve in the following form:

$$\left(\frac{v}{b}\right)^2 (1-A) - 2\frac{v}{b} + (1+B) = 0,$$

$$\text{representing by } B \frac{\left(\frac{db}{dx}\right)^2 x(1-x)}{b^2} = \frac{(n-1)^2 x(1-x)}{(1-x)^2 + 2nx(1-x) + n^2x^2}.$$

Let us seek the points of this curve for which $\frac{d\frac{v}{b}}{dx} = 0$. Such a point lies for the branch of the small volumes on the right of the point for which $\frac{dv}{dx} = 0$, and on the left for the branch of the larger volumes. By differentiating the equation of the curve in the last mentioned form with respect to x , and keeping $\frac{v}{b}$ constant, we find as a condition:

$$-\left(\frac{v}{b}\right)^2 \frac{dA}{dx} + \frac{dB}{dx} = 0,$$

or

$$\frac{v}{b} = + \frac{\sqrt{\frac{dB}{dx}}}{\sqrt{\frac{dA}{dx}}},$$

from which it appears that $\frac{dA}{dx}$ and $\frac{dB}{dx}$ must have the same sign for such points. Now $\frac{dA}{dx} = \frac{c\{a_1(1-x)^2 - a_2x^2\}}{a^2}$ and for $\frac{dB}{dx}$ we find the value $\frac{(n-1)^2\{(1-x)^2 - n^2x^2\}}{(1-x+nx)^4}$. So $\frac{1-x}{x} \begin{matrix} \leq \\ > \end{matrix} \sqrt{\frac{a_1}{a_2}}$ must go together with $\frac{1-x}{x} \begin{matrix} < \\ > \end{matrix} \frac{1}{n}$; or $\frac{x}{1-x} \begin{matrix} \leq \\ > \end{matrix} \frac{1}{n}$ and $\frac{x}{1-x} \begin{matrix} \leq \\ > \end{matrix} \frac{1}{n} \sqrt{\frac{1+\epsilon_1}{1+\epsilon_2}}$ must hold at the same time. What it depends on whether $\frac{dB}{dx}$ and $\frac{dA}{dx}$ is positive or negative, is seen when the value obtained for $\frac{v}{b}$ is substituted in the equation of the curve. If we write this as follows:

$$\left(\frac{v}{b} - 1\right)^2 = A\left(\frac{v}{b}\right)^2 - B$$

we find:

$$\left(\sqrt{\frac{dB}{dA}} - 1\right) = \pm \sqrt{A \frac{dB}{dx} - B} \frac{1}{\frac{dA}{dx}}$$

or

$$\left(\sqrt{\frac{\frac{dB}{dx}}{\frac{dA}{dx}}} - 1 \right) = \sqrt{\frac{A^2}{\frac{dA}{dx}} \frac{d\left(\frac{B}{A}\right)}{dx}}$$

And as $\frac{B}{A} = \frac{(b_2 - b_1)^2 a}{c b^2}$ and $\frac{a}{b^2} = 27 \rho_{kr}$, it appears that $\frac{dA}{dx}$ and so also $\frac{dB}{dx}$ have the same sign as $\frac{d\rho_{kr}}{dx}$. So if $\frac{a_2}{b_2^2} > \frac{a_1}{b_1^2}$ or $\varepsilon_2 > \varepsilon_1$, then $\frac{dA}{dx}$ and $\frac{dB}{dx}$ is positive, and vice versa. The line which divides the angle between the axes into two equal parts in fig. 36 or joins point O' with point O in fig. 37, gives the division between $\varepsilon_2 \gtrless \varepsilon_1$. For $\frac{d\rho_{kr}}{dx} > 0$, $\rho_{kr_2} > \rho_{kr_1}$ or $\frac{a_2}{b_2^2} > \frac{a_1}{b_1^2}$ and $\varepsilon_2 > \varepsilon_1$. This is the case for all points lying right of this line — and the other way about. For the points of this line themselves $\varepsilon_2 = \varepsilon_1$ or $\frac{d\rho_{kr}}{dx} = 0$. But then also $\frac{dA}{dx}$ and $\frac{dB}{dx} = 0$ and so $\frac{x}{1-x} = \frac{1}{n}$, or what is the same thing

$$\frac{x}{1-x} = \sqrt{\frac{a_1}{a_2}} = \frac{1}{n} \sqrt{\frac{1+\varepsilon_1}{1+\varepsilon_2}}$$

But, as we already observed above, this requires that the value l^2 be greater than 1 in the formula $l^2 n^2 (1 + \varepsilon_1)^2 = \left[n + \frac{1 + n^2}{2} \varepsilon_1 \right]$ or $ln(1 + \varepsilon_1) = n \frac{1 + n^2}{2} \varepsilon_1$. Then we have:

$$l = \frac{1 + \frac{1 + n^2}{2n} \varepsilon_1}{1 + \varepsilon_1}$$

or

$$l - 1 = \frac{(n - 1)^2}{2n(1 + \varepsilon_1)} \varepsilon_1.$$

Now for the area OPQ , under the parabola we have

$$(1 + n) \sqrt{\varepsilon_1} \leq n - 1$$

and so ε_1 can become equal to $\left(\frac{n-1}{n+1}\right)^2$ as highest value, and hence

$(l-1)_{max} = \frac{(n-1)^4}{4n(n^2+1)}$. For not very high value of n , $l-1$ is only

small. So $l-1$ is equal to $\frac{1}{40}$ e.g. for $n=2$. For $n=3$, $l-1 = \frac{2}{15}$

But this is no longer the case for high value of n . We need not fear in any case, however, that l will become so great that $a_1 + a_2 - 2a_{12}$ would become < 0 . That c be > 0 , the following equation must hold:

$$2a_{12} < a_1 + a_2$$

or

$$2l\sqrt{a_1 a_2} < a_1 + a_2$$

or

$$2l < \sqrt{\frac{a_1}{a_2}} + \sqrt{\frac{a_2}{a_1}}$$

or

$$2l < \frac{1}{n} \sqrt{\frac{1+\varepsilon_1}{1+\varepsilon_2}} + n \sqrt{\frac{1+\varepsilon_2}{1+\varepsilon_1}}$$

or in our case

$$2l < n + \frac{1}{n}$$

or

$$(l-1) < \frac{(n-1)^2}{2n}$$

Now

$$(l-1) = \frac{(n-1)^2}{2n} \frac{\varepsilon_1}{1+\varepsilon_1}$$

Hence $(l-1)_{max}$ remains also below the value, which would make $a_1 + a_2 - 2a_{12}$ equal to 0.

But now before proceeding to the comparison of the results obtained here with those of the experiment, I shall first have to discuss the question whether the disappearance of the intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$ really involves the disappearance of the complication in the spinodal line, — and so whether the temperature at which the two curves mentioned touch, is at the same time the temperature at which the pair of *heterogeneous* plaitpoints occurring in the spinodal line, coincide. When the points of intersection of the two curves approach each other, the two *heterogeneous* plaitpoints will, no doubt, also come nearer to each other. But it need not follow from this that when the points of intersection coincide, also the pair of plaitpoints coincide. And a priori it is unlikely that this should be the case. The existence or non-existence of points of intersection depends only on properties of the two curves, without a third curve

$\frac{d^2\psi}{dx dv} = 0$ being able to exert any influence on this. But the course of the spinodal line is the result of properties of $\frac{d^2\psi}{dx^2} = 0$ as well as of $\frac{d^2\psi}{dv^2} = 0$ and of $\frac{d^2\psi}{dx dv} = 0$; from this it may already be expected that when the curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ touch, the two *heterogeneous* plaitpoints will occur on the spinodal line, and will lie at some distance from each other. If this is so, this means that the limits for the existence and disappearance of the heterogeneous plaitpoints are wider apart than the temperatures at which the two curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ begin to intersect and stop doing so; and à fortiori this is the case for the limits of the temperature of their appearance and disappearance on the binodal line, and so also for the limits of the temperature for the existence of three-phase-pressure. And that this is true may be seen when we more closely examine the peculiarities which occur in the course of the spinodal line in the case that the two curves still intersect. Let us imagine the circumstances as in fig. 12, Vol. IX, p. 846, Contribution III, viz. the line $\frac{dp}{dx_v} = 0$ at smaller volume than the line $\frac{dp}{dv} = 0$; but preferably at somewhat lower temperature, so that at $x = 0$ the two branches of $\frac{dp}{dv} = 0$ are still separated.

Then the isobars enter the figure at $x = 1$, have $\frac{dv}{dx_p}$ negative, and in the neighbourhood of $\frac{dp}{dv} = 0$ they incline towards this curve which they intersect in a direction parallel to the axis of v . So the quantity $\frac{d^2v}{dx^2_p}$ is positive. For the q -lines the quantity $\frac{d^2v}{dx^2_q}$ is negative in the neighbourhood of $\frac{dp}{dv} = 0$. So in a point of contact of the p - and q -lines, a point of the spinodal line (see Vol. IX p. 747 Contr. II), $\left(\frac{dv}{dx}\right)_{spin}$ is positive according to the formula:

$$\left(\frac{dv}{dx}\right)_{spin} = \left(\frac{dv}{dx}\right)_{p=q} \frac{\left(\frac{d^2v}{dx^2}\right)_q}{\left(\frac{d^2v}{dx^2}\right)_p}$$

And according to the formula Vol. IX p. 749, Contribution II):

$$\left(\frac{dp}{dx}\right)_{spin} = \left(\frac{dp}{dx}\right)_v \left\{ 1 - \frac{\left(\frac{d^2v}{dx^2}\right)_q}{\left(\frac{d^2v}{dx^2}\right)_p} \right\}$$

$\left(\frac{dp}{dx}\right)_{spin}$ has the same sign as $\left(\frac{dp}{dx}\right)_v$, and is therefore negative. In the point of contact the two lines p and q do not intersect. The p -line lies in the point of contact on the same side of the q -line -- e. g. on the lower side. But in fig. 12 contact of a p - and a q -line has again been drawn on the left side of $\frac{d^2\psi}{dx^2} = 0$. But there the p -line

remains above the q -line all through. So there must be a point of contact somewhere between, where there is a transition between these two cases, and where the contact is at the same time intersection. Then not only $\frac{dv}{dx_p} = \frac{dv}{dx_q}$, but $\frac{d^2v}{dx^2_p} = \frac{d^2v}{dx^2_q}$ and so also $\frac{dp}{dx} = 0$.

Then we are in a plaitpoint. If taking due account of the course of the p - and q -lines, we seek this plaitpoint it appears that this point does not lie on that particular q -line that passes through the highest point of the curve $\frac{d^2\psi}{dx^2} = 0$, and has there a direction parallel

to the x -axis, and also possesses there a point of inflection. But it lies on a q -line lying left of the former, where p has a greater value; while this plaitpoint must lie below the point of inflection of the q -line, because $\frac{d^2v}{dx^2_p}$ is always positive.

Of course, but this is not necessary for our argument, if for points of the spinodal line with very small x , the contact of the q - and p -lines is to take place again in such a way that the p -line remains again throughout on the same side of the p -line, which we may also call the lower side, there must exist another plaitpoint also on the left hand of $\frac{d^2\psi}{dx^2} = 0$. So in this second plaitpoint the p -line, coming from the right, must first run above the q -line, which it will touch, and will be below it from the point of contact. What is indeed essential for our argument, is the circumstance that the first-mentioned plaitpoint, the upper of the pair of heterogeneous plaitpoints, which I called the realizable one in a previous Contribution, though it only fully deserves this name when it also lies above the binodal curve, lies on an isobar of higher value of the pressure than the

value of p found in the point in which $\frac{d^2\psi}{dv^2} = 0$ has the smallest volume. And if we now consider the case that the whole closed curve discussed above, has contracted to a single point, and the intersection of the two curves $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$ has disappeared, and the q -line runs parallel to the x -axis in that single point and possesses there a point of inflection, the realizable plaitpoint still exists, and so also the other, the hidden one. A fortiori this is the case when the closed curve still exists, and the intersection of the two curves, $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ has only disappeared because they touch. For then the q -line, which passes through the point of contact, will still possess the points with maximum and minimum volume, and it will lie below the q -line where they have coincided.

So we are justified in the following graphical representation. Let us take an x -axis and a p -axis. Let us construct a figure indicating first the pressure along the liquid branch of the line $\frac{d^2\psi}{dv^2} = 0$, and secondly the pressure along the liquid branch of the spinodal line. Not to interrupt our train of reasoning too much, we shall pass over the other branches in silence, and moreover confine ourselves to the case in which $T_{k_2} > T_{k_1}$. Then the first-mentioned line is a continually descending one. If the temperatures are low — according to the approximate equation of state below $^{27}/_{32} T_k$ — all the points of this line lie below the x -axis. But as we only wish to consider the relative position of the two curves which are to be represented we disregard the absolute height at which we think them drawn. The second line begins and terminates as high as the first, and always remains above it. So in the main it is also a fast descending line. Now if there are on the first line two points, indicating the points of intersection of the line $\frac{dp}{dv} = 0$ with $\frac{d^2\psi}{dv^2} = 0$, the second line will not continually descend, but possess a minimum and a maximum value for p . The minimum value at a value of x which is smaller than the value of x of the first point of intersection, and the maximum value at a value of x , which is greater than that of the second point of intersection. This minimum and this maximum value are those of the pair of *heterogeneous* plaitpoints. If the two points of intersection have coincided on the first-mentioned line, minimum and maximum pressure still occurs on the second. And

only at a temperature, at which either there is not yet question of contact of the two curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2}$, or at which this contact is long over, the complication in the course of the p -line will have disappeared for the spinodal line. At the moment of the disappearance this p -line possesses a horizontal tangent and a point of inflection in the point in which maximum and minimum pressure coincide. If further in such a figure we drew a third line indicating the pressure along the binodal curve, this third line would have a complicated shape — but for this I refer to some Communications occurring in These Proceedings 1905.

But from all this we further conclude that is not necessary that the two curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ intersect for the occurrence of the pair of heterogeneous plaitpoints on the spinodal line. If they only draw near enough to each other, the spinodal line can already possess the described complication, and there can even be three-phase-pressure.

It follows from this that for mixtures the properties of whose components are represented besides by n , by positive ε_1 and ε_2 , the presence of the heterogeneous plaitpoints is not restricted to the space OPQ below the parabola for ε_1 and ε_2 ; but that this space must be extended with a part of the parabola itself — a part lying in the neighbourhood of the top. The theoretically exact shape of this part can only be determined by investigation of the spinodal line itself. But in view of the difficulties attending this investigation, I shall content myself here with an indication of the way in which I have tried to form an idea for myself of the accuracy of my expectations that this part would again be approximately bounded by a parabola, which compared to the preceding one, would have shifted in the direction of the axis, though what follows must not be looked upon as much more than a certain kind of empirical calculation. When the curve $\frac{d^2\psi}{dx^2} = 0$ lies entirely within $\frac{d^2\psi}{dv^2} = 0$, but in the neighbourhood of the latter curve, two other curves, viz. $\frac{d^2\psi}{dv^2} = 0$ at lower temperature, and $\frac{d^2\psi}{dx^2} = 0$ at another still lower temperature will show intersection and contact in the space outside $\frac{d^2\psi}{dv^2} = 0$, where the spinodal curve lies, and where the pair of heterogeneous plaitpoints are found, at a certain distance apart or coinciding.

If in $\frac{d^2\psi}{dv^2} = 0$ we take the lower temperature $T' = \frac{T}{k}$; and in $\frac{d^2\psi}{dx^2} = 0$ the value of the lower temperature $T'' = \frac{T}{k'}$, we obtain by elimination of T , the equation, which with a slight modification agrees with (2) of Contribution X:

$$v^2 \left\{ 1 - x(1-x) \frac{k'}{k} \frac{dx^2}{2a} \right\} - 2bv + \left\{ b^2 + x(1-x) \left(\frac{db}{dx} \right)^2 \right\} = 0.$$

If we now treat this equation in the same way as (a) was treated in Contribution X, we get, for the case that the closed curve contracts to one point, the condition:

$$n - 1 = \sqrt{\left(\varepsilon_1 - \frac{k' - k}{k} \right)} + n \sqrt{\left(\varepsilon_2 - \frac{k' - k}{k} \right)}.$$

So the same parabola as before, only shifted in the direction of the two axes by an amount equal to $\frac{k' - k}{k}$.

The value of T at which the imitated plaitpoints coincide in this calculation, is now k or k' times higher.

(To be continued).

E R R A T U M.

In the proof that the closed curve, the locus of the points of intersection of $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$, always lies at $v < b_2$, a possible case has been overlooked. The value $v < b_2$ may occur if:

$$n - 1 > \sqrt{1 + \varepsilon_1} + n \sqrt{\varepsilon_2},$$

as will be shown in the *Continuation*.



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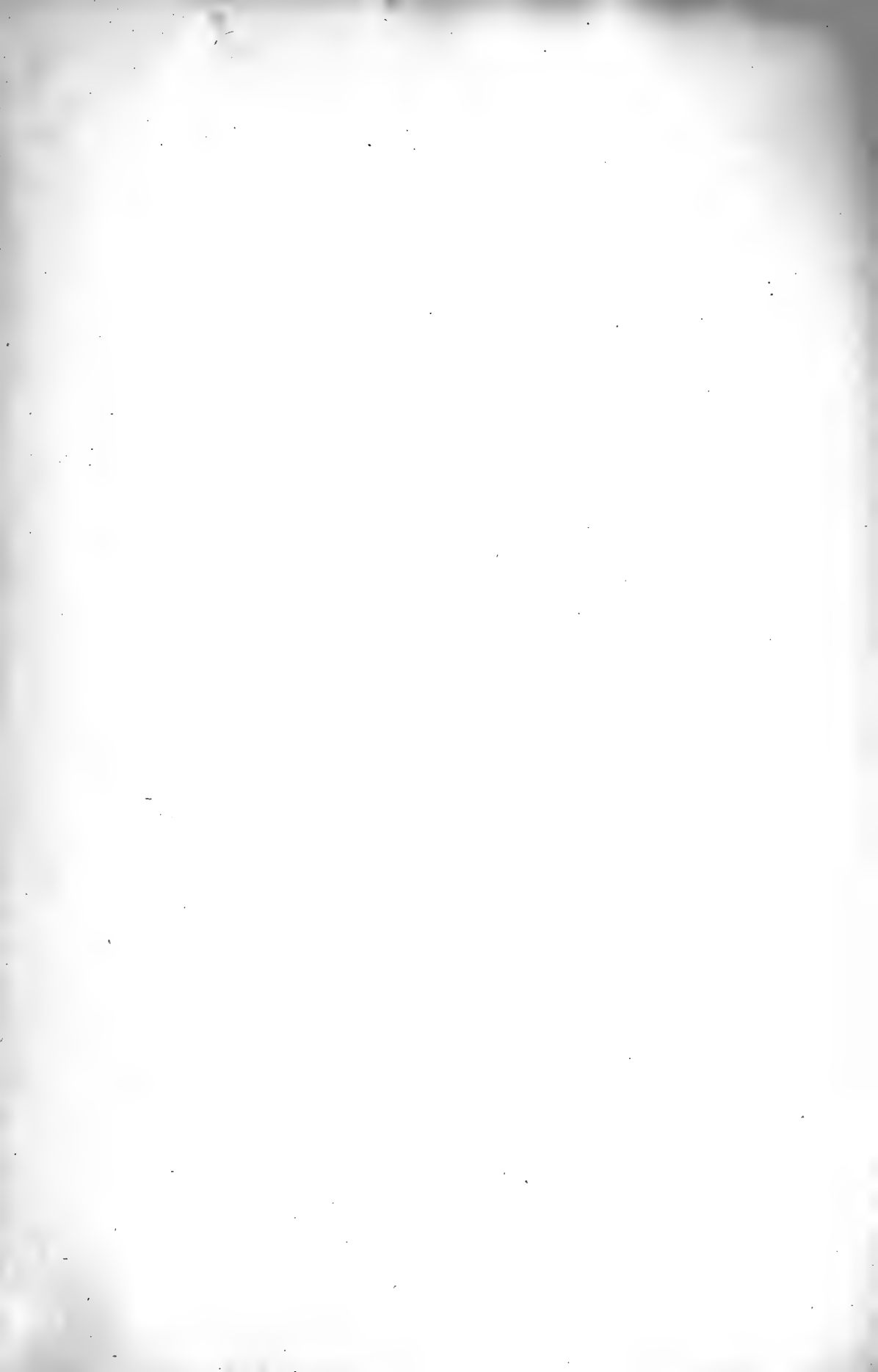
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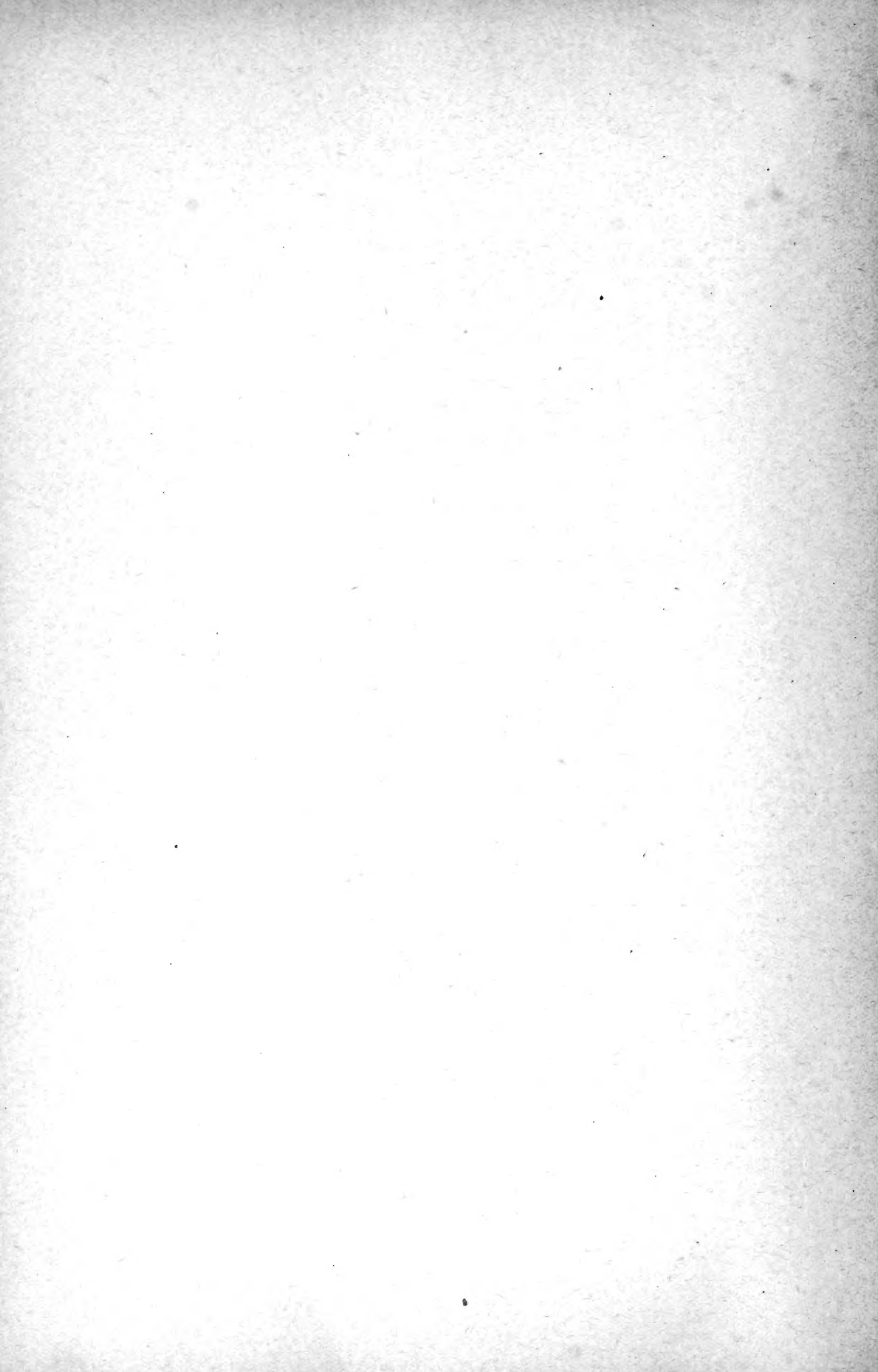
(Translated from: Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige
Afdeling van 30 Mei 1908 tot 28 November 1908. Dl. XVII.)

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